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Dynamic behavior of a distillation tray

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DYNAMIC BEHAVIOR OF A DISTILLATION TRAY

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ABSTRACT

The evolution of a generalized mathematical model to describe the dynamic behavior of a distillation tray has been a subject of considerable interest. Most attempts to formulate a model have resulted in simplified equations, to permit application of the mathematical methods of linear systems analysis. One of the major assumptions made to achieve such a model is that a condition of perfect, or complete, liquid mixing on the trays is representative of the process.

The purpose of the investigation was a study of the effects of imperfect mixing upon the unsteady state behavior of a bubble-cap distillation tray. The research consisted of both an experimental and a theoretical phase.

The tray mixing characteristics were experimentally determined by monitoring the transient response to an inlet liquid disturbance in the form of a non-volatile tracer. The overall dynamic response of the tray to a step-change in composition of the inlet liquid was also experimentally determined for subsequent evaluation of the mixing effects.

Theoretical analysis was chiefly concerned with the evaluation of models which included various liquid mixing assumptions by comparison with the experimentally-determined overall tray composition response. A lumped-parameter model which describes the tray as a single perfectly-mixed stage was included as a basis for comparison. Among the distributed-parameter models which were studied was a system which assumed plug flow of liquid across the tray, and thus constituted the opposite extreme of

no mixing. Two models which represented the case of imperfect mixing between the two extremes were a plug flow model modified to account for eddy diffusion effects and a model based on a series of perfectly mixed stages. These latter two models were developed from analysis of the experimental mixing test results.

The distillation tray was simulated on an analog computer to yield the desired mixing response, by comparison with the experimental response. The simulated response represented a residence time distribution function, which by mathematical treatment produced mixing information in parametric form, such as mean residence time and eddy diffusion coefficient.

The distributed parameter models were found to give satisfactory agreement with experimental results, while the lumped parameter model was found to be the least accurate. Among the distributed parameter models, neither plug flow model, i. e. with or without compensation for diffusion, offered a significant improvement over the series perfect-mixer model.

INTRODUCTION

Modern process control philosophy is directed toward the achievement of the completely automatic chemical processing plant. Integration of the control system with the process into a single operating system requires accurate knowledge of the dynamics of both the control and processing systems. While not many studies of complete plant dynamics have been attempted, a number of individual processes have undergone a thorough study to determine their dynamic operating characteristics.

Studies of dynamic behavior of chemical engineering processes have assumed a role of increasing importance in recent years. Chemical engineers first became interested in process dynamics as analytical methods found application in the design of control systems. Effective employment of the analytical procedures necessarily requires accurate information concerning the unsteady state behavior of the process. A more recent interest in process dynamics is in the field of process design, where a knowledge of process dynamics can be useful in designing equipment.

The theoretical analysis of a chemical operation is most important during the design stage both for optimization of performance and minimization of investment. To theoretically predict the dynamic behavior of a process requires that the separate parts of the overall system, i.e., the measuring element, regulator, controller, and process, all be amenable to mathematical description. Rigorous mathematical models are readily available for all except the process itself.

Development of knowledge of process dynamics has been slow until recent years because of the complexity of the mathematical solutions involved.

The advent of automatic computing machines has done a great deal to remedy the situation. Whereas investigations in the realm of unsteady state presented problems whose solutions were quite formidable, computers have made dynamic studies more commonplace for the engineer.

As one of the most extensively used of the familiar unit operations, distillation has received considerable attention in recent years, to develop an appropriate model to describe mathematically the unsteady state behavior. Distillation column design methods are based essentially on the assumption of steady state operation, and are for the most part empirical in nature. Though such design methods are well-founded and have proven their worth, they are of limited value in the development of advanced process control systems, since nearly all industrial processes are to some extent characterized by unsteady state operation. Much of the early work on the subject of distillation involved batch distillation, which is inherently an unsteady state process. Subsequently, these endeavors have provided an excellent background for later investigations dealing with continuous distillation columns.

While development of a theory of transients in distillation has been emphasized, there is still much to be desired. The material and energy balances of the familiar steady state computations have been extended to include the accumulation of mass and energy, which characterize the unsteady state. Thus, the algebraic equations appearing in steady state design procedures have given way to differential equations. To further complicate matters the resulting equations are non-linear and, therefore, not directly subject to the mathematical methods of linear systems analysis. Confronted by this obstacle, one can either simplify the equations

beyond the point where they represent the actual process to achieve a formal solution, or employ automatic computers to solve the unsimplified equations and obtain a solution for a particular case only. Unfortunately, while both directions have merit, neither has resulted in the true description of the dynamic behavior of a distillation column.

In the absence of a successful mathematical theory, careful experimentation with actual distillation columns under laboratory conditions might be regarded as a substitute for a mathematical solution, if experimental results can be generalized. Dynamic behavior studies generally require specially designed experimental apparatus to provide a sufficient degree of flexibility, and to describe the system response accurately without being confused by the dynamics of auxiliary equipment. Small-scale apparatus is often unsatisfactory in attempting to simulate commercial operations, because a precise knowledge of mass and energy accumulations is required for unsteady state analysis. These factors preclude the use of much of the existing equipment for investigations in the realm of process dynamics. The difficulty in obtaining adequate experimental results has caused a scarcity of data which might be used to verify the many theoretical analyses that have been proposed. Indeed, very few of the mathematical models currently appearing in the literature have been verified experimentally, and often the data presented have been obtained under unique conditions, which prevent attempts to generalize mathematically derived results. A generalized mathematical model to accurately describe the dynamic behavior of commercial distillation systems therefore remains to be achieved. As discussed, the principal difficulty has been the complexity of the operation itself. Underlying this is a lack

of complete understanding of the mass transfer phenomenon as it occurs in stagewise equipment. This is openly reflected in the number of simplifying assumptions, upon which most existing analyses of distillation dynamics have been based. The most common assumptions which have been made are:

1. Molar liquid and vapor flow rates are independent of time.
2. Molar liquid holdups in the column are constant.
3. Vapor holdup is negligible in comparison with liquid holdup.
4. Liquid on the plates, in the reboiler, and in the overhead system is perfectly mixed.
5. Efficiencies of all plates are equal, usually taken to be 100 per cent.
6. The column operates adiabatically.
7. The liquids comprising the binary system have similar thermal properties.
8. The vapor-liquid equilibrium ratio is linear over the range of separations employed.

Many previous research efforts have included other unique assumptions required to effect a solution of their own particular theoretical equations. In his investigations, Voetter (105) studied the influence of the various simplifying assumptions and concluded, rather generally, that errors of 40 per cent were possible. Consequently, a more thorough knowledge of the effects of the simplifying assumptions is necessary to the development of a generalized mathematical model.

Many of the assumptions, while commonly accepted, are recognized as merely approximations. The specific assumptions of perfect, or uniform, mixing on a plate and constant plate efficiency are most frequently applied, but also most usually acceded to be an inaccurate description of the true plate behavior.

Although the existence of a concentration gradient in the liquid on bubble-cap trays was realized as early as 1936, only recently have methods been evolved for predicting both the nature of the gradient and its effects upon column operation as reflected by tray efficiencies. The concentration gradient is a function of the amount of back-mixing that occurs on a plate. If liquid on a tray is completely mixed, the point or local efficiency is the same as the plate efficiency. In practice, and particularly in commercial-size columns, only partial mixing of the liquid occurs, with plate efficiencies greater than 100 per cent being possible. Thus, a proper evaluation of plate efficiencies is directly dependent upon an accurate knowledge of the degree of mixing.

Several concepts have been proposed to describe the liquid mixing process as it occurs on the trays of a stagewise-contacting operation. These have resulted primarily from attempts to uncover the exact relationship between liquid mixing on the tray and plate efficiencies.

Lewis (63) did some of the earliest work in this area, assuming plug flow across the plates. About the same time, a treatment involving several perfectly-mixed pools of liquid was offered by Kirschbaum (54). The pool concept was subsequently revived in the efficiency studies of Gautreaux and O'Connell (35). A recycle stream concept was postulated by Oliver and Watson (74), and Warzel (107), who assumed liquid back-mixing occurs from

the outlet weir to the inlet weir. Johnson and Marangozis (51) carried out some mixing studies on a perforated plate in which splashing of the liquid was considered to be the major mixing process. For predicting tray efficiencies Strand (102) has recently proposed a liquid-vapor by-pass model, in which a fraction of both the liquid and vapor are assumed to effectively pass around the contact zone. The degree of mixing on a bubble plate has also been characterized by measurement of the residence times of liquid elements flowing across the plate, by Foss et al. (33). Finally, the eddy-diffusion concept, employed by Anderson (5), Gilbert (40), Gerster et al. (39) and others, supposes that liquid mixing on a plate can be interpreted by the simple law of diffusion.

It is evident that a wide variety of assumptions concerning the nature of liquid mixing on a distillation tray have resulted, with the true situation being somewhere between perfect mixing and plug flow. In all but the most recent work, only the perfectly-mixed plate model has been employed in the analysis of dynamic column behavior.

The principal aim of the current research project was the determination of the effects of variations in plate composition upon the dynamic behavior of a bubble-cap distillation tray. The overall objectives have been considered twofold, first, the achievement of reliable experimental data and second, theoretical analysis to develop a suitable mathematical model to account for the effects of incomplete mixing of liquid on the tray.

LITERATURE REVIEW

The background for the present work is quite broad, with previous work in a number of diversified categories providing pertinent information relative to the aims of the current investigation. General areas of the literature surveyed preparatory to this study were unsteady state distillation, liquid mixing in continuous flow systems, and liquid mixing on distillation trays.

Several excellent reviews of literature in fields covering the above-mentioned areas have been previously compiled, greatly facilitating the collection of extensive information. Rose and Rose (85) published the most complete treatise of distillation literature for the years 1941-1954, while Gerster (36) abstracted the more recent distillation studies. While these sources are quite comprehensive in nature, attention is focused on those references pertaining to the present work. Archer and Rothfus (6) have recently contributed a comprehensive survey of published literature in the specific area of dynamics and control of distillation columns. Other extensive bibliographies in this area are offered by Rademaker and Rijnsdorp (78), Franke (34), and May (68). Concerning the modern field of liquid mixing, Leonard (59) has composed a thorough review of material on mixing in continuous flow systems, with special emphasis on studies of mixing on a distillation tray.

Batch Distillation

The earliest efforts which involved distillation transient behavior were directed toward a mathematical analysis of batch distillation plate columns. During the course of a batch distillation, the loss of the more

volatile component in the overhead stream causes a corresponding decrease of that component in the still, with the process thereby exhibiting unsteady state behavior. If reflux ratio is constant, a plot of light component concentration in the distillate versus fraction of initial charge distilled would yield an inverted S-shaped curve. The steepness of the middle portion of this distillation curve is an indication of sharpness of separation, which is related in complex manner to the system variables. Consequently, prediction of the distillation curve and determination of sharpness of separation have been the primary subject of the early studies, e.g., Smoker and Rose (100) and Colburn and Stearns (23). However, even when all the usual simplifying assumptions can be made, the distillation curve may be considerably affected by the time lags introduced by the existence of appreciable holdup in the column and auxiliary equipment. Therefore, only solutions of the most idealized cases can be approached analytically.

Rose et al. (79, 81, 82, 83, 84, 88, 90, 91, 92) have made a number of contributions to the development of knowledge of batch distillation, which have provided insight into later work in the area of continuous distillation (80, 89). The results of these investigations collectively represent a very comprehensive study of the various non-idealities which are encountered in batch rectification computations. These efforts which have been supplemented by those of Pigford, Tepe and Garrahan (76) and Huckaba et al. (46, 47, 49) offer possible approaches for handling cases involving:

1. varying relative volatility
2. non-adiabatic column operation

3. plate efficiency less than 100 per cent
4. variation of column holdup with time
5. holdup in accessories
6. various relative sizes of initial charge to still

For detailed description of the effects of these assumptions, examination of the references appearing in the bibliography is recommended.

An excellent summary of equations and method of solution for an idealized case involving constant and equal liquid accumulations on each tray is given by Rose and Johnson (81). Analytical and numerical solution of basic differential equations are discussed and the derivation of finite difference equations, whose application does not require the employment of simplifying assumptions was presented. Rose and Williams (90) earlier showed the advantages of digital computing machines by modifying material balances in cases of appreciable holdup for computer programs. Rose, Johnson and Williams (83, 84) subsequently outlined in detail computational procedures for certain non-idealities to which the usual simplifying assumptions were not readily applied. Pigford et al. (76) solved basic equations, derived earlier by Marshall and Pigford (67), numerically on a large-scale differential analyzer, which is an analog type. Huckaba and Danly (47) developed simple short-cut design techniques for hand calculation and numerical solutions which could be achieved on a medium speed digital computing machine, both approaches assuming constant liquid holdup.

The effects of tray holdup on batch distillation operations have also been studied by a number of other investigators, among the first of which were Colburn and Stearns (23). Huckaba and Tour (49), in their holdup studies, were the first to employ differential energy balances to account

for unequal flow rates between trays. More recently, Bowman and Clark (18) employed an analog computer to simulate a 20-plate batch distillation column for the evaluation of the holdup effects. Rose, Williams and Prevost (92) demonstrated the use of small packed columns to obtain experimental data on the relationship of holdup and sharpness of separation, while Rose, Williams and Kahn (91) further suggested small-scale continuous columns for certain studies of batch distillation. Equations for packed columns differ from those of plate columns by representing holdup in a continuous pattern throughout the column.

Continuous Distillation

Unsteady state behavior, which has been shown previously to be a characteristic of batch distillation, also occurs during the continuous distillation process. Specifically, the two areas of operation which are dynamic in nature are the start-up period prior to attainment of steady state conditions, and the transition period following a change or upset from one steady state condition to another.

The field of isotope separation caused interest in the time to reach steady state at total reflux. Keesom and Van Dijk (53), in some of the earliest work, made a study of isotope separation in a plate column and introduced the concepts of fractional approach to steady state and dimensionless time, which represents the number of changes of liquid holdup on a tray in a given time interval. A number of subsequent studies involving isotope separation have also been concerned with the equilibration time at start-up. Although some of this work was done specifically for packed columns, attention here is limited to those efforts directed toward

analysis of plate columns, among which are the studies of Bartky and Dempster (16), Berg and James (17), Davidson (27), Jackson and Pigford (50), Marshall and Pigford (67), and Montroll and Newell (70).

The isotope separation studies generally employed a series of rather limited assumptions. Only binary component systems operating at total reflux were considered, with further simplifying assumptions among which were the constant molal holdup, constant molal flow rates, negligible condenser holdup, perfectly mixed plates and constant Murphree tray efficiencies based upon vapor compositions. Assumption of a linear equilibrium relationship distinguished most of this early work, thereby avoiding the case of variable relative volatility and the non-linearities which are introduced. Though this latter assumption may be valid for isotope separations, since relative volatility is near unity for these cases, the general applicability of the work is limited.

Bartky and Dempster (16), and Davidson (27) analyzed stripping columns with subsequent solution of differential material balance equations. There resulted a relationship for fractional approach to steady state as a function of time and frequency of column holdup displacement. Berg and James (17) obtained an equation for equilibration time as a function of number plates, relative volatility, and degree of approach to equilibrium. Marshall and Pigford (67) derived equations expressing fractional approach to steady state as an infinite series, each term of which was a function of time, equilibrium constant, plate number, initial liquid composition, and holdup displacement time. Jackson and Pigford (50) examined the previously developed differential material balance equations for the case of

relative volatility differing appreciably from unity. An IBM 701 digital computer was employed to achieve numerical solutions which were compared with solutions of Berg and James, with limitations of such solutions clearly indicated. Montroll and Newell (70), in a purely mathematical treatise, solved non-linear equations describing the time-dependent behavior of a multi-stage cascade separating process based on the Rayleigh equation. Behavior during the transition between stationary modes of operation and the propagation of local concentration fluctuations through the cascade were studied.

Lapidus and Amundson (58) extended the concepts of Marshall and Pigford (67), who had developed the basic differential material balance equations for binary distillation in plate columns, into a complete solution of the unsteady state for a general equilibrium relationship, with constant feed rates. Acrivos and Amundson (1, 2) presented solutions to the problem considered by Lapidus and Amundson which were accomplished by means of a Reeves electronic analog computer, both for the case of a linear vapor-liquid equilibrium relationship and the case of a non-linear relationship. An alternate approach to a solution using matrix methods was also considered by Amundson (4).

Rose and his co-workers (80, 81, 89), especially Williams, following up their work in batch distillation made some important contributions toward the understanding of the problem of transient behavior of continuous columns. The basis has been the familiar differential-difference equations employing a relative volatility equilibrium relationship with most of the usual simplifying assumptions, including perfect mixing of liquid on the trays. Computations were carried out on both an IBM 650 digital computer

and a Reeves electronic analog computer. Rose and Williams (89) present one of the earliest methods to account for liquid and vapor flow dynamics. The method of lumped parameters was employed, which requires actual column data to achieve a numerical solution; however, no comparison with experimental work was offered.

Analog computer solution to the problem of column response to a step change in feed composition, as studied by Rose et al. (80), was similarly examined by Lafyatis (56) with employment of the alternate linear equilibrium relationship. Davis (29) employed the Whirlwind computer at M.I.T. to solve a similar problem with the same assumptions as Rose et al.

In later work, Williams et al. (109, 110, 111, 112) were more specifically concerned with development of an optimum automatic control scheme for a continuous distillation column. The work is summarized in a report by Williams (109) in which he clearly defines the control problem and suggests several approaches to achieve optimum control. Williams, Hartnett and Rose (112) investigated the effects of varying feed rates, imperfect sampling and varying reflux conditons. Analysis of column control based on feed rate disclosed that step changes of feed composition were most disturbing and consequently a system which adequately controlled composition changes could handle feed rate changes.

Rademaker and Rijnsdorp (78) were also concerned with the problem of column response from control system viewpoint and discuss the significance of various assumption. It is incidentally concluded that variations in internal flow rates must be considered by applying enthalpy balances.

Rosenbrock (93, 95, 96) presents a discussion of the general problem of distillation plate column dynamic behavior, including the application of

the various simplifying assumptions. Examination of available methods of solution led Rosenbrock to conclude that digital computing machines offered greatest advantage. Several digital computer solutions were presented (94) for equilibration time at total reflux and for step change in feed composition of binary continuous distillation columns. The usual simplifying assumptions were employed, however, non-linear equilibrium relationships were studied. Although Murphree vapor efficiencies of less than 100 per cent were included, they were assumed constant. The existence of non-perfect mixing of liquid on a tray in commercial size columns is mentioned, but no mathematical provision for degree of mixing was offered.

Voetter (105) studied analytically the concentration response of a column to step changes in feed composition. The treatment is similar to that of Marshall and Pigford (67) with the usual simplifying assumptions, a linear equilibrium relationship and a constant stripping factor being employed. The theory of small perturbations was applied with the use of Laplace transforms. The resulting equations for predicting the transient response of column compositions were functions of the residence times and number of plates. A discussion of the relative significance of the simplifying assumptions employed is included, with the rather general statement that they may lead to errors as large as 40 per cent. Experimental data were obtained on a column of the laboratory Oldershaw sieve type, with concentration step changes introduced into the reflux and vapor feed streams. The experimental results indicated that the response of fractionating column to concentration disturbances can be fairly well described by the theoretical model, even in its simplest form.

Armstrong and Wilkinson (7, 8, 9) contributed by their investigation of response of a 4-inch diameter, five-tray column to step changes in vapor composition to the bottom plate, and step changes in feed composition to a 4-inch diameter, 21-tray column. Analytical solutions were again based upon the usual simplifying assumptions in conjunction with either a linear vapor-liquid equilibrium relationship, or with a relationship approximated by two straight lines. The computed solution also utilized measured steady state tray efficiencies. It should be noted that the application of Laplace transforms in the analytical procedures necessitated linear equations. An important feature of this work is the experimental phase, which satisfactorily confirmed the analytical solutions. It was also concluded that the experimental time-composition curves conform to the theoretical predictions of Voetter and the digital computations of Rosenbrock. A discussion of the assumption of perfect mixing of tray liquid indicates apprehension concerning its validity in columns larger than four inches in diameter.

Armstrong and Wood (10, 11, 12) conducted further studies employing the theoretical model advanced earlier by Armstrong and Wilkinson. In the first of these works (12) more simplified expressions are derived for the initial phase of the transient period and which could be extended throughout the complete range of transition of the column to steady state. The range of applicability of the earlier work on response of plate compositions to step changes in feed composition was thereby increased. In later efforts (11), the effects of step changes in reflux and vapor flow rates for cases of both constant feed plate composition and varying feed plate composition were investigated. It is noted that assumption of constant

feed plate composition considerably simplifies the boundary conditions and subsequently the solution. The study resulted in a means of approximating boundary conditions for varying feed plate composition. Results compared favorably with the experimental data. It was further noted that the transient response of the pilot column to a step change in reflux rate is similar to exponential decay. In another paper (10) a simplified model is investigated by frequency response techniques in an effort to extend the dynamic analysis. The usefulness of such methods arises at high frequencies, at which column response is difficult to evaluate by transient response techniques. High frequency analysis is, however, important for study of a loop closed by an automatic controller.

Huckaba, Franke and May (34, 48, 68) propose a model for predicting response of a continuous distillation column to step changes in feed composition and reflux ratio, separately or simultaneously, as well as changes in reboiler heat duty. Most of the usual simplifying assumptions are applied with the principal exceptions being the use of energy balances between stages and empirical relations to describe the vapor-liquid equilibrium and tray efficiencies. Analytical procedures involved numerical analysis on an IBM 650 digital computer and yielded results which agreed with experimental data from a ten-inch diameter, twelve-tray column. These efforts are an extension of the earlier work by Huckaba and Danly (47) similarly conducted for batch distillation, and which included experimental data on the same column operated batchwise. Although perfect mixing of liquid on the trays was assumed for simplification, Franke (34) and May (68) both recommend study of the effects of degree of liquid mixing upon transient behavior of the column. Huckaba (46) has also presented an excellent

generalized summary of the mathematical analysis involved in studying the behavior of holdup in mass transfer operations.

Lamb, Pigford and Rippin (57) formulated an approach to the problem of predicting frequency response and transient behavior of a distillation plate column employing the linear, small perturbation types of equations. The principal advantages of this method of analysis is the applicability of the whole body of theory of linear differential equations. The usual simplifying assumptions were applied with the exception of equal molar overflow and constant molar liquid holdup. Results of an analog computer simulation of a five-plate column and a sixteen-plate column are presented as frequency response data calculated from transient response data using Fourier transform techniques. Due to irregularities in the data for the five-tray system, only a rough agreement with the earlier results of Armstrong and Wilkinson is obtained.

Baber et al. (13) experimentally investigated the effects of a step change in reflux composition to the top tray of a column operating at total reflux. The column employed was a two-foot diameter, five-plate column which had previously served for the A.I.Ch.E. tray efficiency studies at the University of Delaware (39). An extensive range of both vapor and liquid flow rates was used. Later study on the same column by Baber and Gerster (14) was concerned with column response to a step change in liquid rate in the reflux stream or in vapor rate to the bottom tray. The experimental composition-time curves agree favorably with predicted values based on analog computation using the perturbation equations of Lamb et al. (57). The first study demonstrates that the transient response could be predicted in the absence of rate equations, while the second study indicated the

ability to predict the response to rate changes. An interesting facet of the studies is the agreement of the analytical and experimental results, based upon a model assuming perfect mixing of tray liquid, although Gerster et al. (39) had previously determined liquid flow across the tray was more nearly in plug flow. The use of the perturbation equations also permitted the assumption of average values for the slope of the pseudo-equilibrium curve for each plate, which is necessarily a more realistic situation than had been used previously.

Harper (43) has conducted the only study which attempted to account for the effects of incomplete mixing of liquid on the trays upon the dynamic response of a column. An analog computer simulation of composition dynamics was based upon the concept advanced by Kirschbaum (54) that each tray could be represented by several perfectly mixed pools of liquid. Employing equations developed by Gautreaux and O'Connell (35), Harper determined that two pools of uniformly mixed liquid would adequately represent each tray in the previously mentioned University of Delaware column, which contained five, two-foot diameter bubble-cap plates. Perturbation type equations, similar to those of Lamb et al. (57) were formulated for the analytical phase. The conclusion was reached, following comparison with experimental data, that the perfect mixing assumption did not appreciably alter the predicted solution when compared with the case of two pools of uniformly mixed liquid. These results are mentioned briefly in the report of Baber et al. (13). It is further interesting to note that Baber and Gerster (14) working with the same column, nevertheless, found it expedient to assume two perfectly mixed pools for the top tray and uniform mixing across the remaining trays to accurately predict column response. This

compensation grew out of difficulties caused by cold reflux entering the top tray and which resulted in predicted response based upon a perfectly mixed tray being greater than the experimental response.

Recently, Wages (106) employed analog computer simulation methods in a further analysis of the perfect mixing assumption. Changes in reflux composition were imposed upon a five-tray column to evaluate the time-dependent concentration behavior as predicted by two distinct models based upon different mixing assumptions. The first was a lumped parameter model, based upon the uniform-mixing assumption, yielding a set of linear ordinary differential equations. The second was a distributed parameter model based upon assumption of plug flow of liquid across the length of the tray, which generated a set of linear partial differential equations. Dynamic behavior was analyzed not only by transient studies, but by pulse testing and frequency response techniques as well. While no experimental work was conducted, the models were compared with experimental data of Baber et al. (13, 14). The lumped parameter model was found to represent the experimental behavior better than the distributed parameter model. However, comparison of the two models indicated significantly different results, which led to the conclusion that the actual condition of mixing on a distillation tray must be given consideration.

Liquid Mixing

Examination of the literature pertaining to study of the unsteady state response of distillation plate columns has therefore revealed that little information exists concerning theoretical models which include the

effects of incomplete mixing of liquid on the trays. Although nearly all investigators employed perfect mixing assumptions, at the same time they suggest further study of this mathematical simplification. While Harper did not find great differences from assuming incomplete mixing, it can hardly be concluded that mixing effects are generally insignificant. Further, most of the response studies discussed herein contain experimental results from relatively small diameter columns, for which assumption of perfectly mixed tray liquid may be nearly correct. Certainly, this cannot be safely extended to assume that larger commercial-size columns can be similarly treated. More specifically, O'Connell (73) suggests that for liquid paths less than ten feet the number of perfectly mixed stages is roughly equal to the number of feet traversed by liquid across the tray.

Lack of knowledge concerning liquid concentration gradients on distillation trays also posed a major problem in attempts to accurately correlate plate efficiencies for large diameter trays. The assumption of liquid being completely mixed due to turbulence created by vapour bubbling leads to the Murphree vapor point efficiency, E_{oG}, being identical with the overall Murphree vapor plate efficiency, E_{MV}. When the effectiveness of mixing is reduced, as in the case of large trays, the average liquid concentration is somewhat less than the exit liquid concentration. Subsequently, for this situation, E_{MV} based upon the exit concentration is higher than E_{oG} based upon average tray liquid concentration. Manning, Marple and Hinds (66) in mass transfer efficiency studies of a five-foot diameter distillation column, with bubble-cap plates, presented data indicating the overall plate efficiencies. Thus, incomplete mixing has a sizeable effect upon tray efficiencies.

Efforts to determine the relationship between liquid mixing on the tray and plate efficiencies have produced valuable information pertinent to a fundamental description of tray behavior. Several concepts have been proposed to characterize the liquid mixing effects upon the trays of a plate column.

The early work of Lewis (63) acknowledged liquid concentration gradients in trays of only a few inches in diameter, even up to superficial vapor velocities of six feet per second. Concluding from this that liquid mixing on a large tray is incomplete, Lewis derived a relationship between point and overall plate efficiencies, based upon assumptions of liquid in plug flow across the tray and completely mixed vapor flow, as follows:

$$E_{MV} = \frac{1}{\lambda} (\exp \lambda E_{oG} - 1) \qquad \text{where} \qquad \lambda = \frac{mG}{L} \qquad 1$$

$$E_{MV} = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \qquad 2$$

$$E_{oG} = \frac{y - y_{n-1}}{y^* - y_{n-1}} \qquad 3$$

m = equilibrium line slope
L = molar liquid rate, lb-mol/hr-sq ft
G = molar vapor rate, lb-mol/hr-sq ft
E_{MV} = Murphree vapor plate efficiency
E_{oG} = Murphree vapor point efficiency
yi = vapor composition on ith plate
y* = equilibrium vapor composition

Additional assumptions employed were local efficiency constant across the plate, linear equilibrium relationship for the range of tray compositions, and constant molar flow ratio, L/G. Also considered were cases in which no longitudinal mixing occurs in either liquid or vapor, liquid flow in one case being in parallel direction with flow on adjacent trays, and in the

alternate case in opposing direction. Of the three cases considered, parallel flow gave highest overall plate efficiencies, while the lowest efficiencies resulted from the counter-flow situation. It should be noted that a plug-flow model represents totally unmixed liquid, the opposite extreme of a perfectly mixed model.

In another early reference, Kirschbaum (54) suggested the division of a tray along the direction of liquid flow into several equal-sized perfectly mixed pools of liquid. A tray with a single pool of course, represents perfect mixing, while an infinite number of pools is tantamount to assuming plug flow. No method was offered for determining the number of discrete pools of liquid for a given tray.

Gautreaux and O'Connell (35) recognized that the condition of no liquid mixing is as unrealistic as is the perfect mixing assumption and that length of liquid path influences the degree of mixing. They employed the pool concept of Kirschbaum and derived a relationship between plate and local efficiencies using the assumptions of Lewis, with the exception of the liquid being in plug flow. The equation was presented as follows:

$$E_{MV} = \frac{1}{\lambda}\left(1 - \frac{\lambda E_{OG}}{n}\right)^n - 1 \qquad \text{where } n = \text{no. stages} \qquad 4$$

As a means of estimating the number of perfectly mixed stages per tray, n, a tentative correlation with length of liquid path is presented. When n=1, a condition of perfect mixing exists for which the above equation yields $E_{MV} = E_{OG}$. Similarly, when n becomes large, a condition of plug flow is approached and the above reverts to the Lewis equation.

A more recent use of the Kirschbaum pool concept was made by Mickley, Gould and Schwartz (69) who proposed frequency response testing as a possible experimental technique for simultaneous determination of liquid mixing

characteristics, plate efficiencies, vapor-liquid equilibrium, and liquid holdup on a single bubble tray. The simplifying assumptions employed in the mixing model were identical to those of Gautreaux and O'Connell. Mathematical analysis used to interpret the measurements is based upon a linearized model, despite which, systems with non-linear equilibrium curves are adequately represented. Systems with significant enthalpy effects, however, presented mathematical difficulties which prevented quantitative interpretation of the frequency response measurements for the case of incompletely mixed tray liquid. Determining operating plate characteristics from measurements of a response to random fluctuations in normal input quantities during commercial operation was discussed as an ultimate goal. Such a technique would, of course, eliminate the need for artificial disturbances, but the feasibility of such methods necessitates prior understanding of system response to sinusoidal perturbations, i.e., frequency response.

Oliver and Watson (74) proposed a fractional mixing parameter, F, to describe incomplete mixing on a tray. The mechanism of mixing involved was not explicitly stated, but assumes back-mixing from the outlet weir to the inlet weir. The determination of values of the parameter was achieved by sampling both immediately preceding and following the inlet weir. Based on experimental values for F overall Murphree vapor plate efficiency, E_{MV}, can be determined from the "true" Murphree vapor point efficiency, E_{oGt} , to the proposed relationship:

$$E_{MV} = \frac{\exp \lambda\,(1 - F)E_{oGt} - 1}{\lambda(1 - F)} \qquad \text{when} \quad F = \frac{x_w - x_i}{x_o - x_i} \qquad \begin{matrix} 5 \\ 6 \end{matrix}$$

Only a very rough correlation of the mixing parameter with operating variables was achieved and was presented in graphical form. The results from

their 18-inch tray indicated that for several systems studied, the mixing was generally between one-quarter and three-quarters complete. It is noted that when mixing is complete, F = 1 and $E_{MV} = E_{oGt}$, while for plug-flow, F = 0 and the Lewis equation holds. Due to the existence of eddies near the weirs, experimental errors in these results may be significant. Also presented is a discussion of limitations of such efficiency correlations due to the assumptions inherent in the two-film theory of mass transfer. Principal among these is the assumption of uniform mixing of liquid in the vertical direction, effects of which are discussed by Thorogood (103).

Warzel (107) took an approach similar to Oliver and Watson, in which he described the liquid mixing mechanism as represented by a hypothetical recycle of liquid from the exit weir to the inlet weir. The resulting equation was identical to the relationship of Oliver and Watson. In accordance with their previous study, fractional mixing was shown to increase proportionately with vapor flow. Warzel recommended application of the recycle model for prediction of efficiencies on small diameter trays only, and suggested a distribution function approach should be investigated for the case of larger trays.

Johnson and Marangozis (51) submitted a liquid mixing factor, β, contingent upon splashing of liquid to correlate the degree of liquid mixing on a tray. Actual splashing measurements were made on a 36-inch by 3-inch perforated plate, and results correlated with several operating conditions. Only a thin layer of liquid was observed on the tray accompanied by a considerable froth layer, therefore the amount of liquid mixing by diffusion in the axial direction was considered negligible. Employing this mixing factor, a relationship between E_{MV} and E_{oG} was again presented, as follows:

$$E_{MV} = \frac{E_{oG}\left[1 - \exp(-\theta_1 S_o)\right]}{\theta_1 S_o} \qquad 7$$

where $$\theta_1 = \frac{1}{2\beta} - \left[\frac{1}{4\beta^2} + \frac{\lambda E_{oG}}{\beta S_o}\right]^{\frac{1}{2}} \qquad 8$$

and $$\beta = 0.688(10^{-4})\, u_G^{2.15}\, u_L^{2.29}\, h_w^{4.2}\, \nu_L^{-0.57} \qquad 9$$

S_o = total length traybubbling area, inches
u_G = linear gas velocity, based on bubbling area, ft/sec
u_L = linear liquid velocity, ft/sec
h_w = exit weir height, inches
ν_L = liquid kinematic viscosity, sq ft/sec

The experimental results were found to be represented better by the Lewis equation due to the small mixing factors which prevailed. Experimental efficiencies for a bubble-cap plate appearing in the literature were, however, predicted quite well by the splashing model. The use of the splashing model equations for predicting tray efficiencies was recommended only for systems where splashing is significant and again where vertical liquid mixing is complete.

Crozier (24) has presented another continuous mechanism for axial dispersion of liquid which is associated with splashing of liquid. A mixing parameter, γ, which is apparently based on a modified Prandtl-Taylor mixing length mechanism, as follows:

$$\gamma = 0.40\left[\frac{(u_G)^{\frac{1}{2}}}{h_c^2 L_w}\right]^{0.074}\left[\frac{b}{S_o}\right] \quad \text{(without splash baffle)} \qquad 10$$

u_G = superficial linear vapor velocity, ft/sec
h_c = clear liquid height, inches
L_w = liquid rate, ft^3/inch weir width
b = plate width, inches
S_o = active tray length, inches

A relationship between E_{MV} and E_{oG}, similar to that of Oliver and Watson, and Warzel is offered as:

$$E_{MV} = \frac{(1-\gamma)}{\lambda} \left[\exp \frac{\lambda E_{oG}}{(1-\gamma)} - 1 \right] \qquad 11$$

Experimental measurement of liquid concentration gradients was achieved by imposing a step change in the form of a dye solution into an air-water system. The transient dye concentration on the tray, and the following decay to the original steady state were analyzed. A range of values for γ is reported as from 0.5 to 1.5. Crozier criticized the efficiency relationship of Oliver and Watson, and Warzel, pointing out that the inlet boundary condition did not adequately represent the concentration "jump" at the inlet weir. Leonard (59), in a later study, indicates that Crozier likewise has not properly accounted for boundary conditons, and notes the similarity of the efficiency relationship with those of the earlier works. Leonard further criticizes the implication of a turbulent diffusion concept, which avoids a term, proportional to the second derivative of concentration with respect to distance, characterizing the well-known diffusion equation.

Wehner and Wilhelm (108) present a good discussion of generalized boundary conditions for flow reactors, which includes dividing a reactor into three zones, allowing a different axial diffusion coefficient for each. Van der Laan (104) extended the three zone concept to the case of a non-reacting flow section operating under transient conditons.

Anderson (5) employed an eddy diffusivity concept to characterize tray liquid mixing in formulating a solution to an unidimensional steady state version of the diffusion equation:

$$\frac{dx}{ds} - \left(\frac{D_E h_f b\, L}{L}\right) \frac{d^2x}{ds^2} = -\left(\frac{G\, b}{L}\right)(y_n - y_{n-1}) \qquad 12$$

with the inlet boundary condition:

$$x_{n+1} = x\Big|_{s=o} - \left(\frac{D_E h_f b\, L}{L}\right) \left.\frac{dx}{ds}\right|_{s=o} \qquad 13$$

h_f = liquid foam height
b = plate width
L = liquid molal density

Further assumptions included in the model are:

1. constant point efficiency along tray length
2. linear vapor-liquid equilibrium line
3. well-mixed and uniformly distributed vapor flow
4. uniformly distributed liquid flow
5. no liquid concentration gradient perpendicular to flow

Based on experimentally measured diffusion coefficients, previously obtained at Massachusetts Institute of Technology, a relationship is obtained between E_{MV} nad E_{oG}. The rather cumbersome expression which was also presented graphically is given as:

$$(1 + E_{MV}) = \frac{1 - \frac{1}{2M}(M - \Delta)}{1 - \left(\frac{M - \Delta}{M + \Delta}\right) \exp \tfrac{1}{2}(M - \Delta)} \qquad 14$$

$$= (M^2 - 4M\,\lambda E_{oG})^{\frac{1}{2}} \qquad 15$$

$$M = \left(\frac{S_o L}{D_E h_f b\, \rho_L}\right) \qquad 16$$

The model was not experimentally evaluated.

Gilbert (40) also solved a uniaxial diffusion equation quite similar to that of Anderson. A mixing parameter was determined, for both bubble-cap and sieve trays, by a comparison of theoretical and experimental frequency responses. The theoretical frequency response is based upon digital computer solution of a tray-transfer function originally derived and discussed

by Kramers and Alberda (55) for a continuous flow system, assuming constant longitudinal diffusivity. The experimental frequency response study was accomplished on a one-foot wide plate with three feet active length. A dye solution was injected with a sinusoidal time-variant concentration and output dye concentrations were observed. Various operating conditions were imposed upon the tray. The degree of mixing, which was found to vary only slightly with liquid and vapor rates, was characterized by a modified dimensionless Peclet number, Pe, as follows:

$$Pe = \left(\frac{S\,u_L}{D_E}\right) \quad ; \quad \left(\frac{D_E}{h_c u_L}\right) = C_1 \left(\frac{hf}{h_c}\right)^{C2} \left(\frac{1}{u_L}\right)^{C3} \qquad 17$$

for bubble-caps: $C_1 = 0.9$, $C_2 = 2.4$, $C_3 = 0.4$

for sieve trays: $C_1 = 0.25$, $C_2 = 3$, $C_3 = 1$

Based upon the above-mentioned mixing parameter, solution of the steady state diffusion equation yields a rather complex exponential-quadratic expression relating E_{MV} and E_{oG}, given as:

$$E_{MV} = \frac{1}{4p}\left[(1+p^2)\exp\frac{-Pe}{2}(1-p) - (1-p^2)\exp\frac{-Pe}{2}(1+p)\right] - 4p \qquad 18$$

$$p = \left(1 + \frac{E_{oG}}{Pe}\right)^{\frac{1}{2}} \qquad 19$$

A graphical solution is also given by Gilbert, which appears to be identical to the solution of Anderson.

Gerster et al. (39) in the final report of the University of Delaware study of tray efficiencies for the A.I.Ch.E. presented another model describing the rate of liquid mixing as a longitudinal eddy diffusivity, D_E. A correlation for D_E using 3-inch bubble-caps is presented as follows:

$$D_E^{\frac{1}{2}} = 0.0124 + 0.0171\, u_G + 0.0025\, L_w + 0.0150\, h_w \qquad 20$$

u_G = linear vapor velocity, ft/sec
L_w = liquid volume flow rate factor, gal/min-ft weir width
h_w = exit weir height, inches

Liquid mixing results of Foss et al. (33) for sieve trays were shown to produce diffusivities nearly equal to those for 3-inch bubble caps. Again recommended to characterize the degree of mixing is the dimensionless Peclet number, Pe, which is the ratio of the distance traveled by the liquid, S, to the mixing length, D_E/u_L:

$$Pe = \left(\frac{S\, u_L}{D_E}\right) = \left(\frac{S^2}{D_E t_L}\right) \qquad 21$$

u_L = linear liquid velocity across tray, ft/sec
t_L = average liquid residence time on tray, sec
S = distance traveled by liquid across tray, ft
D_E = longitudinal eddy diffusivity, sq ft/sec

Solution of the one-dimension steady state diffusion equation employing boundary conditions discussed by Wehner and Wilhelm (108) resulted in the following relationship between E_{MV} and E_{oG}:

$$\frac{E_{MV}}{E_{oG}} = \frac{1 - \exp(n + Pe)}{(n+Pe)\left(1 + \frac{n-Pe}{n}\right)} - \frac{\exp n - 1}{n\left(1 + \frac{n}{n+Pe}\right)} \qquad 22$$

$$n = \left(\frac{Pe}{2}\right)\left(1 + \frac{4\, E_{oG}}{Pe}\right)^{\frac{1}{2}} - 1 \qquad 23$$

Numerical solutions were worked out on a digital computer and presented graphically. A steady state tracer technique was employed to evaluate the diffusion coefficient experimentally. For a tray with no mass transfer between the gas and liquid phases, the homogeneous diffusion equation:

$$\left(\frac{1}{Pe}\right)\frac{d^2x}{dw^2} - \frac{dx}{dw} = 0 \qquad 24$$

yields the following solution:

$$\left(\frac{x - x_i}{x_g - x_i}\right) = \exp wPe \qquad 25$$

where:

w = fraction of distance from exit to inlet = S/S_o
x = liquid concentration at any point w
x_i = inlet liquid concentration
x_g = liquid concentration at injector grid

Non-volatile tracer is injected into the froth just upstream of the exit weir and tracer diffusion upstream determined by equations as shown. Experimental studies on a rectangular bubble-cap tray 14 inches wide by 31 inches long, employing air-water and steam-water systems, substantiated the diffusion correlation.

Harris and Roper (44) in studies of performance of a 12-inch diameter sieve tray report that the A.E.Ch.E. correlation for back-mixing (3), also reported by Gerster et al. (39), underestimates the degree of mixing on the plate used. Hence the equations based on the correlation would tend to predict lower liquid efficiencies than might be expected.

Barker and Self (15), using the same mathematical and experimental analysis as Gerster et al. (39) investigated liquid mixing on a sieve plate and reported the following diffusion coefficient correlations:

$$D_E = 0.01298\ u_G^{1.44} + 0.3024\ h_c - 0.0605 \qquad 26$$

$$h_c = 0.078 + 0.00145\ L_W + 0.031\ h_W - 0.013\ u_G \qquad 27$$

u_G = linear superficial vapor velocity, ft-sec
h_c = clear liquid height, ft
L_W = liquid flow rate, gal/min-ft weir width
h_W = exit weir height, inches

Additional correlations for diffusion coefficient involving froth momentum, h_f, were given as:

$$\left(\frac{2D_E}{u_f h_c}\right) = C_1 \left(\frac{h_c u_f}{h_f}\right)^{-C_2} \qquad 28$$

where: for 1-inch weir: $C_1 = 0.0024$, $C_2 = 3.02$

for 2, 3, 4-inch weir: $C_1 = 0.0098$, $C_2 = 2.91$

$$h_f = 0.116 + 0.00395\, L_w + 0.088\, h_w + 0.0384\, u_G \qquad 29$$

A comparison of experimental values for D_E with those predicted by the correlation of Gerster et al. (39) for bubble-cap trays exhibited some scatter. The above equations, however, were not able to resolve slight deviations from data of Foss et al. (33) and Gilbert (40), also working with sieve trays.

An interesting observation was the pulsation of liquid froth at high vapor velocities, 7 ft/sec, which apparently increased values of D_E, apparently indicating a corresponding increase in degree of liquid mixing. McAllister and Plank (65) previously reported periodic pulsation of froth in an air-water system on sieve and bubble-cap trays at air rates of 6 ft/sec. For a bubble-cap tray with a liquid path of 11.5 inches, the pulsing increased the number of well-mixed pools, calculated by methods of Gautreaux and O'Connell (35), thus indicating a decrease in the degree of back-mixing.

The eddy diffusion concept offers a definite advantage by representing the liquid mixing as a continuous mechanism, compared to the discrete stage models. Limitations of the diffusion models arise from the inability to describe trays which are characterized by a significant degree of channelling or stagnation of liquid.

Strand (102) most recently proposed a model for prediction of plate efficiencies, which accounts for liquid and vapor bypassing the contacting

zone. Assuming a fraction of liquid, β, and a fraction of vapor, ϕ, effectively pass around the active tray area, overall tray efficiency was related to point efficiency as follows:

$$E_{MV} = \frac{(1 - \phi)\, E_{MV}'}{1 - \beta\ \lambda E_{MV}' \left(\frac{1 - \phi}{1 - \beta}\right)} \qquad 30$$

$$E_{MV} = 1\ \frac{(y_n' - y_{n-1})}{(y_n^{*\prime} - y_{n-1})} \qquad 31$$

where primed values represent actual contacted phases. The calculation of the bypass factors was achieved by comparing a Murphree vapor plate efficiency, E_{MV}, calculated via empirical correlations presented by Gerster et al. (39) with an experimentally determined Murphree vapor plate efficiency, E_{MV}', based on actual contacted phases. The experimental work was carried out for several systems on a tray with a 3-foot square active tray area employing 4½-inch bubble caps. Experimental tray efficiencies were compared with values predicted by both the A.I.Ch.E. design correlations and for the cases where a correction for bypassing had been included as a modification. The agreement was decidedly improved upon compensation for liquid bypassing, while a vapor bypass correction did not enhance the results. The bypassing of liquid was observed to occur primarily through the vapor space at high vapor flows, and at low vapor flows along the periphery of the tray.

While a bypass mechanism offers a definite method for improving upon the results of the diffusion model, this particular approach of Strand must be recognized as highly empirical. More specifically, determining the bypass factor from the discrepancy between experimental and predicted

efficiencies does not allow for other errors, e.g., in the diffusion correlation itself.

Most of the previously discussed references attempted to evaluate the liquid mixing mechanism from its effects upon tray performance. An alternate approach is direct measurement of mixing effects. One means discussed by Gerster et al. (39) is through accurate information on the concentration profile of liquid on the active tray. Efficiencies might be related directly according to the expression:

$$\frac{E_{MV}}{E_{OG}} = \int_0^1 \frac{(x - x_i^*)}{(x_o - x_i^*)}\, dw \qquad 32$$

w = fractional distance from outlet to inlet
x_i^* = inlet equilibrium liquid composition
x_o = exit liquid composition
x = liquid composition at any point on tray

A second method of direct analysis of mixing mechanism is based on a knowledge of the residence times of the liquid elements flowing across the tray.

The basis of this method of approach is the assumption that some portions of the liquid flow remain on the tray longer than others. Theoretically, there will exist a complete range or distribution of residence times, with zero and infinity as possible limits. For plug flow all liquid elements reamin on the tray an equal length of time, while for perfect mixing a large segment of the liquid will have left the tray prior to the average residence time.

The residence-time concept found early application, e.g., MacMullin and Weber (64), in 1935, discussed residence time distributions of a series of continuous flow stirred-tank reactors. However, the concept was not

widely used until 1953 when the comprehensive treatment of Danckwerts (25) appeared, dealing with residence time distribution studies of continuous flow systems. A detailed analysis of the fundamentals is included with discussion of application to several types of continuous processes. As generally described, distribution of residence times for a continuous flow system, such as a distillation tray, were determined by injecting a pulse of non-volatile tracer into the inlet liquid and measuring tracer concentration in the outlet liquid as a function of time. The residence time distribution function, rtdf, is given by the relationship:

$$F(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \qquad 33$$

where $F(t)dt$ is the fraction of liquid remaining on the tray for a time interval between t and t - dt, and $C(t)$ is the concentration of tracer in the outlet liquid as a function of time. A step change in tracer concentration may be made as a substitute for a pulse, with $C(t)$ then being acquired as the time-derivative of the concentration-time function of tracer in the outlet liquid. An implicit assumption of these techniques is that the tracer particle behave as any other fluid element. If molecular diffusion of the tracer is considerable, the assumption may not hold.

Foss et al. (31, 33) determined the degree of mixing for a sieve plate by experimental measurement of the distributions of residence times of tray liquid. An expression relating plate efficiencies to these distribution functions is derived as:

$$\frac{E_{MV}}{E_{oG}} = \frac{1 - \int_0^\infty F(\theta)\exp\ \theta E_{oG}\, d\theta}{\lambda E_{oG} \int_0^\infty F(\theta)\exp\ \theta E_{oG}\, d\theta} \qquad 34$$

The relationship reduces to the well-known equations for tray efficiencies

for the cases of no mixing or complete mixing. Plate efficiencies were actually measured under conditions for which rate of liquid mixing and point efficiencies had been previously determined. Residence time experiments consisted of tracer injection as a unit step input, to avoid difficulties inherent in achieving a sharp pulse. The plate used for the study was a 36-inch long by 9.5-inch wide rectangular sieve tray, employed in a previous study by Foss and Gerster (32). The experimental rtdf data, in conjunction with measured values of the mass transfer coefficient, permitted computation of liquid concentration profiles and plate efficiencies to check the derived expressions. Predicted mass transfer rates were found to be somewhat high.

The actual rate of liquid mixing was found to be linearly related to the rate of increase of variance with liquid path, or second moment, of the distribution function. The rate of increase of variance was shown to be related only to the bulk momentum of flowing froth and liquid holdup per unit tray area. It can also be expressed in terms of an eddy diffusion term. Both expressions are given as:

$$\frac{d\sigma_t^2}{dw} = 2.057(10^{-3})\, h_c(\rho_f u_f)^{-2.8} = \left(\frac{2D_E}{u_f^3}\right) \qquad 35$$

σ_t^2 = variance or second moment of rtdf
D_E = eddy diffusion coefficient, sq ft/sec
ρ_f = froth density = h_c/h_f
u_f = mean linear froth velocity, ft/sec

The froth momentum correlation necessarily assumes a constant rate of increase of variance. A qualitative analysis of rtdf data indicated incomplete mixing, with mixing rate increased at lower froth velocity. Bypassing is apparently indicated near the liquid inlet only. This would seem to point out the value of the residence time concept for being able to

describe all conditions of mixing on a tray, whatever the mixing mechanism.

Leonard (59) has criticized the unnecessary complexity of the derivation given by Foss (31) upon which the above reference is based. The implicit assumptions, which are not easily recognized, are listed by Leonard as:

1. constant local efficiencies
2. uniform interfacial area
3. uniform vapor ditribution
4. completely mixed vapor flow
5. small net transport rate relative to moles fed
6. linear equilibrium line

Leonard (59) more recently presents another investigation of liquid mixing on a bubble-cap tray employing a residence-time concept. The value of this reference is in the detailed review and analysis of the distillation tray liquid mixing problem. Experimental determination of residence time distribution functions for a rectangular distillation tray 8.875-inches wide by 17.75-inches long active area, employed 19 rows of $\frac{1}{2}$-inch bubble caps. A sinusoidal time-variant dye concentration was imposed upon the inlet liquid stream. The system permitted steady state mass transfer while analyzing unsteady state dye concentrations in the exit stream.

An expression for volumetric liquid holdup, H_L, is presented as a function of mean residence time, t_L:

q = steady volumetric inflow rate
θ = relative time - t/t_L
$F(\theta)$ = residence time distribution function rtdf

$$H_L = q^{t}L = \int_{o}^{\infty} \theta F(\theta)\, d\theta \qquad 36$$

The limitation of assuming that only convection causes transfer of tracer across the boundaries is imposed, as implied by Levenspiel and Smith (62). Spalding (101) discusses the additional complicating assumption of diffusion of tracer across the boundary. The holdup expressions of Van der Laan (104) for plug flow with diffusion in an infinitely long pipe, assuming constant Peclet number, Pe, are given for comparison:

$$q\, t_L = H_L\left(1 + \frac{2}{Pe}\right) \qquad 37$$

or

$$H_L = q\, t_L - \frac{2D\, A^2}{q} \qquad 38$$

where A = cross-sectional area of liquid flow.

A dispersion parameter was presented as a function of dimensionless variance, σ^2, and the number of cap rows perpendicular to axial liquid flow:

$$n = N_R \hat{\sigma}^2 \qquad \text{where} \qquad \sigma^2 = \sigma'^2/t_L \qquad 39, 40$$

The residence time distribution function for the experimental trays was approximately represented by a Poisson distribution, whose dimensionless variance is given by:

$$\hat{\sigma}^2 = \left(\frac{7\, u_G^2\, g}{N_R}\right) = \frac{7\ (\text{"F"-factor})}{N_R} \qquad 41$$

and:

$$\hat{\sigma}^2 = 2/Pe \qquad \text{where } \sigma'^2 \text{ is small.} \qquad 42$$

Combining equations, an empirical relation for eddy diffusion coefficient results:

$$D_E = 3.5(u_G^2 \rho_g)\, S_R\left(\frac{q}{h_c b}\right) \qquad 43$$

S_R = axial distance between cap rows
h_c = clear liquid height
b = tray width
q = volumetric liquid inflow rate
u_G = superficial vapor velocity
ρ_g = vapor density

The third moment of the observed rtdf does not equal the third moment of either a uniaxial diffusion model or a series-mixer model. The third moment, a measure of skewness, is concluded to be necessary along with the first and second moments, or mean and variance respectively, to uniquely describe a dispersion model. The major conclusions were that no presently used mixing model adequately predicts the rtdf to be expected from the system, and that no method yet exists which employs the rtdf to accurately relate point and overall tray efficiencies.

In addition to the references cited concerning mixing models and residence time concepts, a number of other contributions have been made in these areas, dealing with continuous flow systems. Some of these references are noted, if only briefly, for their potentiality or importance to the development of mixing concepts.

Buckler and Breitman (20) presented data, not previously available, for the number fraction distribution of residence times of particles in fluid passing through a series of up to 75 zones of perfect mixing. The theory is reviewed and extended to include recycle.

Cholette and Cloutier (22) define models for various mixing conditions in continuous flow systems. Differential equations are derived to account for an effective volume of mixing, short-circuiting, holdup time, partial displacement, or piston-flow. The values of different factors are included in an integrated equation which can be experimentally determined from system response to a feed composition disturbance.

Danckwerts (26) extended the discussion in an earlier reference (25) to include determination of an "average age" as indication of stagnation, and channeling by a conversely "low age". Zweitering (114) further

extended the concepts of Danckwerts on degree of mixing and segregation to the case of a continuous flow system with an arbitrary, but known, rtdf. A life expectation distribution, an age distribution, and a condition of maximum mixedness are defined. Hanratty (42) subsequently related the lifetime distribution and age distribution.

Levenspiel (61) studied problems of choosing and fitting mixed models, which consisted of interconnected regions with various modes of flow. Such models might be employed to represent real vessels, in which flow deviates greatly from plug-flow.

Hanhart, Kramers and Westerp (41) analyzed the rtdf of gas passing through an agitated gas-liquid contactor of 0.6 meter diameter, and found that in the region of effective agitation the rtdf closely resembles that of a perfect mixer.

Debaun and Katz (30) used probability distribution of Chi-square statistics to approximate rtdf's for a class of mixing systems, to solve certain transient analysis problems and to smooth random inlet concentration fluctuations. Moment-generating functions for a cascade of perfect mixers is discussed. Katz (52) investigated the problem of smoothing out concentration fluctuations by passage through a cascade of stirred-mixers from a statistical viewpoint. The theory of random processes, involving both covariance function techniques and spectral function techniques, is applied in the formulation.

Naor and Shinnar (71) recently presented a new method for representation of residence time variability in continuous flow systems, which is based on an intensity function. This approach permits some insight into the mechanism of the mixing processes within the system and aids in the

interpretability of experimental curves.

Wolf and Resnick (113) recently proposed an "F-function" which can be employed to represent residence time distribution for real systems. The function can account for dead-space, bypassing, error in mean residence time, lag in response or a combination of the foregoing.

Otto and Stout (75) discussed description of mixing dynamics by taking moments of a system time response, thereby making the assumption of a specific model unnecessary. A mixing parameter was offered as the ratio of the square of the first and second moments. Leonard (59), however, has shown that the third moment is required in addition, to provide a unique representation.

Further work on the residence time concept and the diffusion model approach has been presented in studies of mixing in various types of process equipment, notably reactors, packed beds and pipes. While much of interest may be contained in such references, they are considered somewhat beyond the scope of the present investigation and are not discussed here.

EXPERIMENTAL INVESTIGATION

Experimental System

The binary system of acetone and water was chosen to analyze distillation transients. The system has a large vapor-liquid equilibrium ratio (see fig. 1), with no azeotropes, making possible a wide difference in composition through the column. This permitted a column with a minimum number of trays, thereby simplifying column dynamics by eliminating time lags. A large concentration gradient across the tray could be attained, which permitted liquid mixing effects to be more easily detected. Another factor considered was composition analysis. The acetone-water system was quite adaptable to a refractive index analysis, which was easily carried out. As a liquid-phase controlling mass transfer system, the temperature and heat energy requirements for distillation were reasonable. The economic considerations also favored the acetone-water system, as opposed to an organic binary system which would also have presented recovery problems.

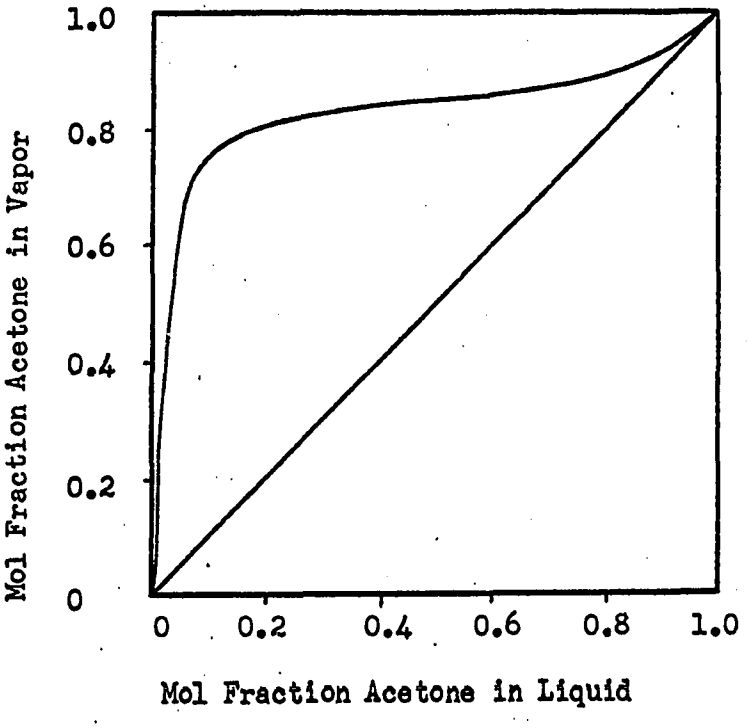
Among the disadvantages were a non-constant relative volatility, and the prevention of using plexiglas construction in the column due to its solubility in acetone.

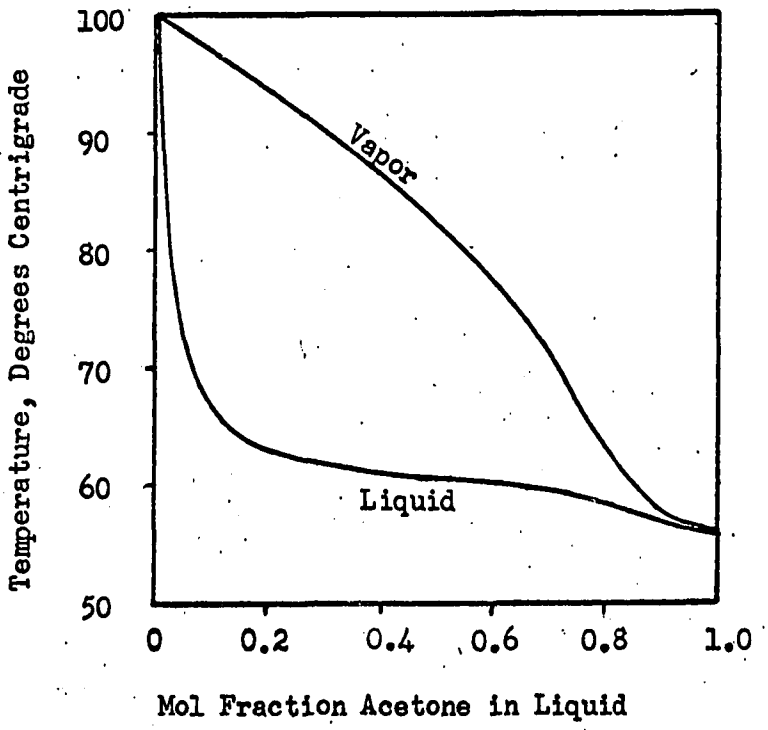
Equipment Design

The experimental assembly was specifically designed, within economic limitations, to produce the desired information on dynamic behavior of a distillation tray. The basic feature of the apparatus was a rectangular tray of suitable size to allow liquid concentration gradients to exist in the longitudinal direction, i.e., along the liquid path. The overall plate

Fig. 1. Acetone-water binary system
a. Vapor-liquid equilibrium diagram

b. Temperature composition diagram


1.0
0.8
0.6
0.4
0.2
0
Mol Fraction Acetone in Vapor
0
0.2
0.4
0.6
0.8
1.0
Mol Fraction Acetone in Liquid


100
90
80
70
60
50
Temperature, Degrees Centrigrade
Vapor
Liquid
0
0.2
0.4
0.6
0.8
1.0
Mol Fraction Acetone in Liquid

measured 9 inches by 20 inches, which though modest in comparison with many commercial tray sizes was considerably greater than most laboratory-sized columns. A practical limitation involved here was the allowable heat duty, which determined the condenser and reboiler requirements. While rectangular cross-section is not a common design feature of industrial columns, a number of distillation tray efficiency studies (5, 24, 33, 40, 59, 103) have employed such columns. The basic advantage is a greater liquid path for a given tray area. Previously, results achieved on a rectangular tray have been extended to larger trays by considering the experimental tray as a section of a larger one. Although the effects of flow along the periphery of a circular tray were not considered, the study of longitudinal composition gradients was facilitated.

The overall design resulted in a two-tray column (see table 1, figs. 3,4), with the lower tray providing vapor distribution to the upper tray, which constituted the test tray. The column was constructed of flanged sections, which provided a degree of flexibility, in that the plates were removable and additional sections could be added if desired. Each tray contained eleven 2-inch diameter bubble-caps (see fig. 5), which were chosen because they have found extensive application in the chemical industry and permitted a wide range of operating conditions. An adjustable exit weir, extending across the full width of the plate, was provided for each tray. Attached to the exit weir was a baffle-type downcomer, with a cross-section 9 inches by 1 inch, extending down to within 1 inch of the tray below. The tray spacing was 22 inches, which provided ample distance to minimize the effects of liquid entrainment. The test tray was provided with 15 permanent sample taps, each consisting of a 12-inch length of 3/16-inch O.D. copper

Table 1. Tray design characteristics

Bubble cap	number per tray	11
	tray layout	triangular pitch
	cap spacing	5-inch base, 4-inch altitude
	diameter, O.D.	2 inches
	height above tray	2 inches
	metal thickness	1/32-inch aluminum
Slot	number per cap	25
	height	27/32 inch, up 5/32 inch
	width	tapered 3/32 to 3/16 inch
	area per cap	2.97 sq. inches
Riser	diameter, O.D.	1 3/8 inches
	height above tray	1 1/2 inches
	metal thickness	1/32-inch copper
Active Tray	width	9 inches
	length	18 inches
	exit weir width	9 inches
	exit weir height	variable
Downcomer	width	9 inches
	length	1 inch
	height above tray	1 inch
Nominal design rates		
	allowable heat duty	350,000 BTU/hr
	superficial linear vapor velocity	2.3 ft/sec
	vapor flow rate	180 cfm
	liquid flow rate	0.8 gpm

Fig. 2. Schematic flow diagram of column assembly and accessory equipment

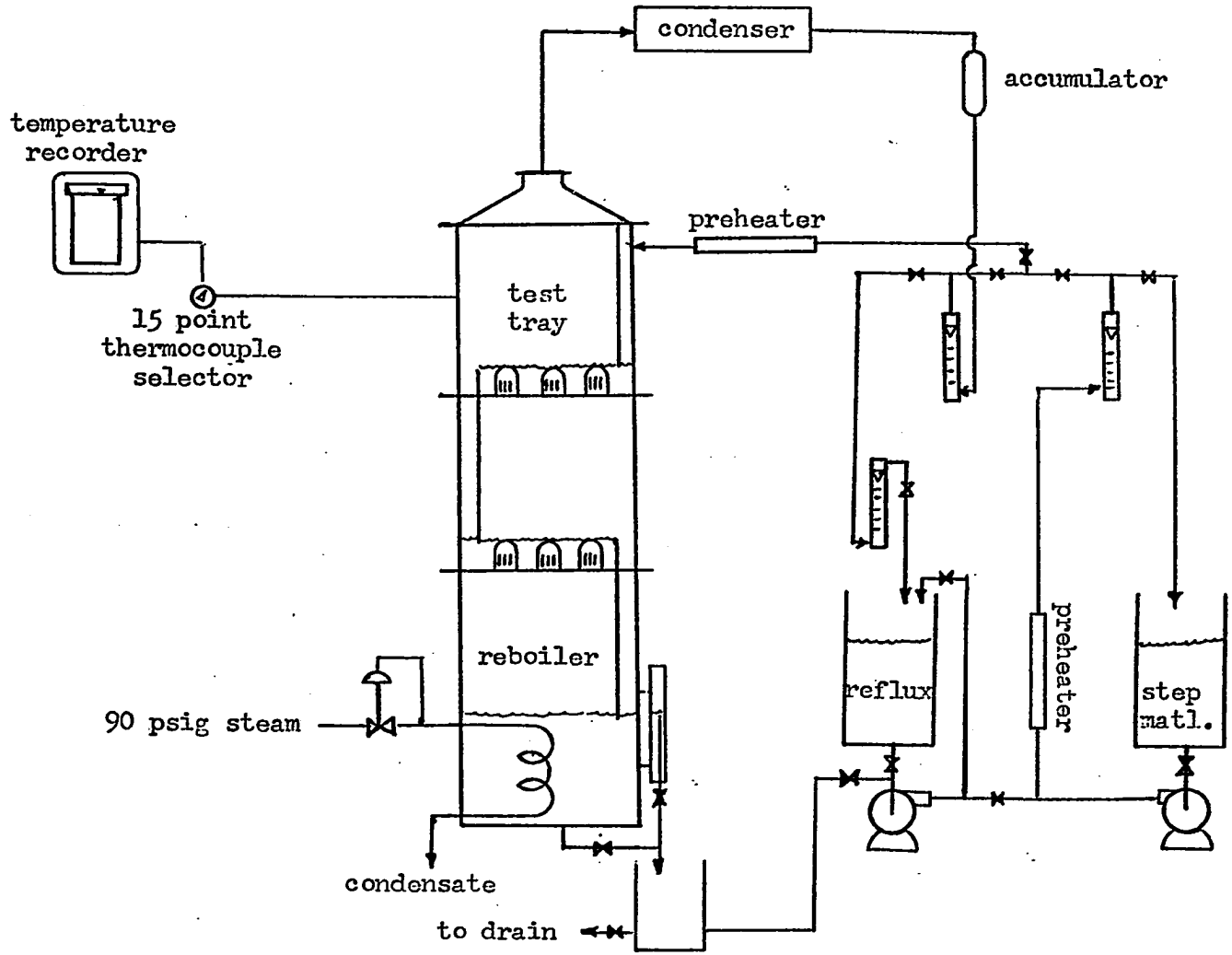
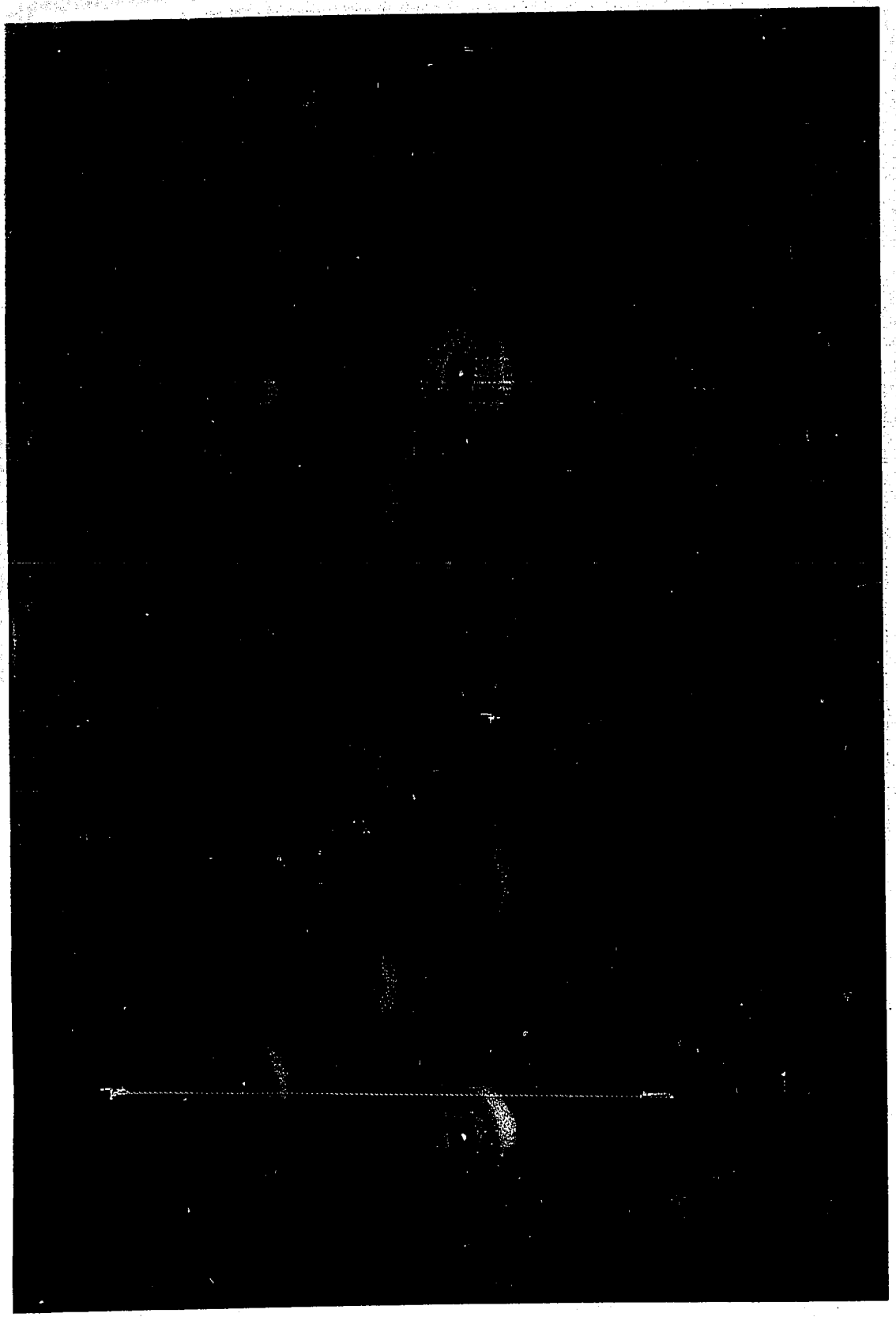

condenser
accumulator
temperature recorder
preheater
test tray
15 point thermocouple selector
reboiler
90 psig steam
reflux
preheater
step matl.
condensate
to drain

Fig. 3. Completed column assembly

Fig. 4. Column during assembly

Fig. 5. Experimental tray during construction



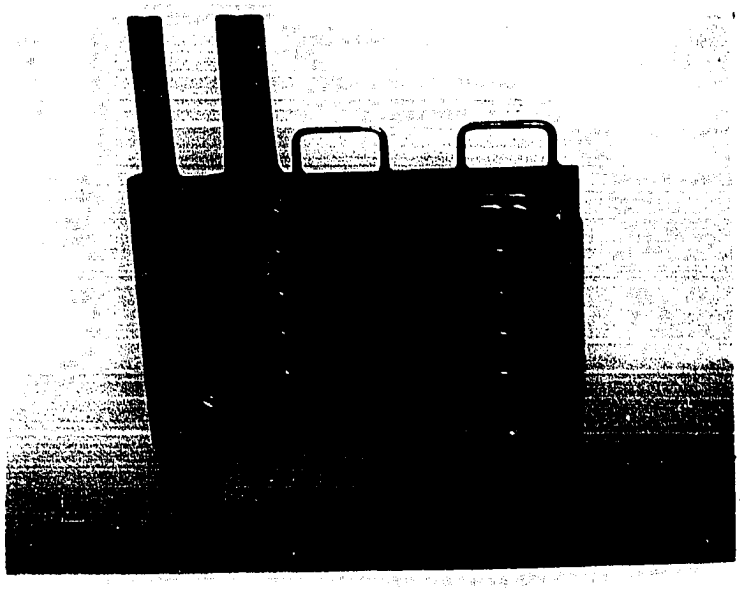
tubing. The sampling positions were arbitrarily chosen along three rows parallel to liquid flow. The taps protruded approximately 3/16 inch above the tray floor, with the opposite end extending through the column wall. The test section was also fitted with two 5-inch by 9-inch glass windows on opposite sides of the column to observe tray operation. Fittings were also provided in both tray sections for insertion of a probe for additional liquid or vapor sampling. Material of construction employed for the entire column was 1/8-inch mild steel, with the exception of the trays which were 1/4-inch mild steel. The column was completely insulated with a 2-inch layer of styrofoam insulation covered by 5-mil corrugated aluminum sheeting.

Energy was supplied to the column via four plate coil heaters installed in the reboiler section below the lower tray (see figs. 6,7). The heaters have an effective heat exchange area of 12 square feet, and were fed with 90 psig saturated steam through a pressure control valve. The reboiler had a cross-section identical to that of the column itself, but is 36 inches deep to permit disengaging space above the heaters. An adjustable dip leg was provided to vary the liquid level in the reboiler.

The condenser consisted of four ten-foot long sections of 3-inch I.D. glass-lined concentric pipe exchanger tubes, in parallel, with total effective heat exchange area of 24 square feet. Aapor lines to the condenser were 3-inch O.D. copper pipe, traced by 5/16-inch copper tubing which carried steam, and covered by a 1-inch layer of fiberglas insulation. Liquid lines from the four condenser tubes are 1/2-inch copper tubing and are manifolded shortly downstream to a vented accumulator, which was formed

Fig. 6. Panel coil heater

Fig. 7. Reboiler internal assembly viewed from above



from a 1-foot section of 2-inch schedule 40 steel pipe.

Various temperatures were monitored by iron-constantan thermocouples, and individually recorded on an adjustable range (0-100 mv.) potentiometric recorder.

Three stainless steel drums provided for collection of reflux and bottoms when necessary and for preparation and storage of liquid fed to the column to provide the desired upset. The reflux drum and stepchange liquid drum outlets were each connected to an Eastern Motors model D-11 pump. These were each manifolded to provide recirculation, transfer between drums, or feed to the column from either drum. Rotameters were provided on both the reflux line leading from the accumulator and the step-change liquid recycle line. An additional rotameter was provided on the reflux line to the collection drum permitting partial reflux operation of the column if desired. Preheaters, each of which consisted of a 2-foot section of 1/2-inch inner tube concentric pipe exchanger, were provided on both the column return line and on the step-change liquid recycle line. Each was heated on the shell side by pressure-regulated steam. The preheaters were installed because of difficulty in controlling condenser outlet liquid temperature of the liquid returned to the column was maintained near the tray temperature to avoid the effects upon mass transfer due to addition of sub-cooled liquid.

All liquid piping not otherwise described consisted of 1/2-inch schedule 40 steel pipe. The reflux line from the accumulator and the step-change liquid recycle line were joined to the column return line at the control panel. Both lines were provided with plug-cock valves which permitted on-off type flow adjustment for quick introduction of the upset

liquid. At the column itself the liquid return line was split into a four point distributing manifold of 3/8-inch copper tubing connected to the column wall at a level 20 inches above the tray floor. Upon entering the column at this point, liquid was allowed to drain to the tray below between the column wall and a downcomer baffle which separated the liquid from the tray vapor flow.

Experimental Methods

General

During both the mixing and composition transient phases of the investigation the column was operated under conditions of total reflux. To facilitate use of mixing results in the formulation of a model for composition transient description, similar operating conditions were maintained for both phases of the study. Two levels of reflux, or inlet liquid flow rate, were employed with similar concentration profiles across the tray.

The specific liquid mixing characteristics of the test tray were determined for each steady state level by maintaining operating conditions, but replacing the reflux stream with a stream of similar composition and flow rate but containing a non-volatile dye. This provided, in effect, a step-change in the color of the test tray inlet liquid, which initially was colorless. Sample streams from several locations along the tray length were monitored, for a colorimetric analysis, over the whole time interval during which steady dye concentrations were approached. This technique was similar to that of Foss et al. (33) and offered the advantage of direct measurement of mixing characteristics while actual mass transfer conditions

were maintained. It must be noted, however, that Foss et al. and Gilbert (40) employed simulated distillation systems to study mixing effects across a single tray. There was some precedent in that Leonard (59) did employ an actual operating binary distillation system in frequency response mixing studies of a bubble-cap tray.

The measurement of the dynamic response of the tray to a composition change was accomplished by operating the column initially at the chosen steady state level. Following the attainment of steady operating conditions, the reflux stream was replaced by a stream of different composition with volumetric flow maintained at the same rate. The step-change in tray inlet liquid composition, thus induced, caused an upset in tray liquid compositions, which was monitored by sampling at several locations along the tray length for the duration of the upset. A subsequent refractive index analysis of the samples was made to determine the time-composition relationship for the interval during which unsteady state mass transfer conditions were imposed.

Column operating procedure

The initial steps included filling the reboiler and trays, from one of the inventory drums, with liquid containing a moderate amount of acetone; adjusting valves for total reflux; and turning on maximum cooling water flow to the condenser. Controlling reflux liquid temperature by condenser cooling water flow adjustment resulted in early difficulties of partially condensed reflux. Subsequently, preheaters were installed to allow better temperature control and totally condensed reflux. Liquid level in the reboiler was maintained, by adjusting a dip leg tube, to cover the heaters by a minimum of 2 inches of liquid, thereby allowing approximately 20 inches

of disengaging space.

The steam flow to the reboiler was then turned on and adjusted to the desired pressure by set-point adjustment of the control valve. The approach of the column to steady state was monitored by recording column temperature on the recorder. By means of a test lead connected to the thremocouple switch, and a glass thermometer, the recorder was calibrated prior to each run to read temperature directly in degrees centigrade. As the column neared steady conditions, steam was turned on to the vapor tracing line and to the preheater on the column return line. The pressure regulator on the preheater steam line was adjusted to maintain column feed liquid temperature slightly below tray temperature. Temperature control at this point was critical since a low temperature caused sub-cooling effects upon the tray mass transfer, while a high temperature caused flashing of the feed liquid as it entered the column.

Following attainment of steady state, which normally was a matter of several minutes, samples of the test tray concentration profile were taken for immediate analysis. If needed a small amount of make-up liquid containing a greater amount of acetone was added, and samples again taken at steady state. Upon reaching desired column conditions, samples of reflux, inlet and outlet vapor were also taken. At this time step-change liquid was prepared corresponding to the mixing or transient run to be made. For the composition transient, this was merely an acetone-water solution of desired composition. The mixing tests, however, required further addition of a non-volatile dye to act as a tracer. A deep purple dye was achieved by adding equal 2-ounce quantities of red and blue food coloring per 50 gallons of acetone-water solution. The step-change liquid was then

recirculated through the rotameter and the flow rate adjusted to match the observed flow of reflux liquid. The steam to the preheater on the step-change liquid recycle line was turned on and adjusted by pressure regulator. The recycling liquid temperature was maintained equal to the "cold" reflux liquid temperature. When the sampling equipment was prepared for use, the step-change liquid was quickly introduced to the column return line, via the plug valves at the control panel, at the same time diverting condensed distillate flow to the appropriate collection drum. The length of a run, of either type, was approximately six minutes. At the completion of the run, the valves were again adjusted for total reflux, in preparation for another run or column shutdown.

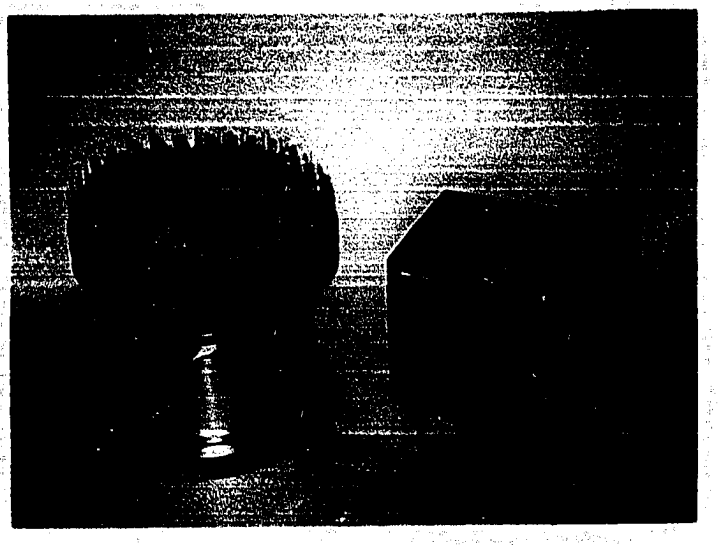
Sampling procedure

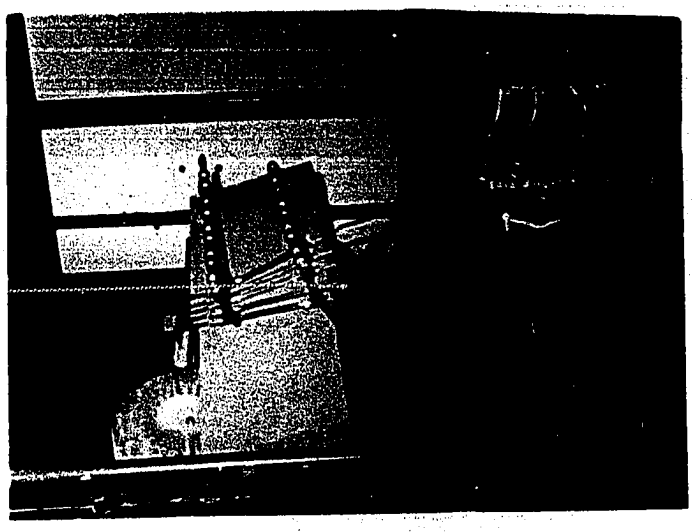
Sampling of the liquid from the various tray locations was accomplished with the aid of an automatic fraction collector (see figs. 8, 9). This device consisted of a perforated circular table, in which 150 test tubes (13x100 mm) were inserted, and which could be rotated at a prescribed time interval as small as three seconds. As many as five samples could be taken at one time, thereby permitting a complete tray length profile to be taken. By a series of samples at discrete time intervals, the changes in composition with time were evaluated.

The temperature of the liquid to be sampled was approximately 60 degrees centigrade, which necessitated cooling of samples to prevent evaporation losses. The length of the sample line was to be kept at a minimum to avoid large time lags in sampling. To achieve effective cooling in a short distance, a manifold of five individual sample coolers of the concentric tube type were constructed (see fig. 9). Each cooler consisted of

Fig. 8. Automatic fraction collector

Fig. 9. Sample collection system





3/16-inch copper inner tube and a 3/8-inch copper outer tube, with an overal length of 8 inches. Countercurrent flow of cooling water was applied to the shell side.

Liquid flow rate in the sample lines was controlled at the desired level, 20-30 ml/min, by nozzles made from 3-inch lengths of thick-wall glass capillary tubing.

The sample cooler manifold was attached to the appropriate series of sample taps prior to each run, by short lengths of tubing. Maximum cooling water flow to the coolers was turned on. The proper sampling interval was set on the timer unit, with the fraction collector. Generally, a 12 or 15 second interval was employed for the composition transient tests, while the mixing tests required a 20 second interval. The longer interval was necessitated by the larger quantity of liquid required for analysis. The fraction collector table was normally not attached until sampling was imminent, to avoid contamination. The test tubes, while mounted in the table, were washed in an automatic lab washer and rinsed with distilled water prior to each run.

When the proper column conditions were reached, the sampling was begun by removing tubing clamps from the sample lines to start flow. When flow was ascertained to be satisfactory, the timer unit was switched on and at least one set of samples taken at the initial steady state. Then, noting the time relative to the sampling system, the step-change was introduced to the column by adjusting valves at the control panel. To prevent evaporative losses and contamination, rubber stoppers were manually inserted into the test tubes as they were filled.

Since the column was under slight pressure, no special equipment was necessary to withdraw vapor samples from the column. A long section of 3/16-inch copper tubing was employed as a probe, and was attached to a sample cooler to condense the vapor sample as it was drawn off.

Analytical procedure

For the mixing tests a Bausch and Lomb Spectronic 20 colorimeter, was employed to analyze dye concentration of the samples. The particular size test tubes employed were capable of being inserted directly into the colorimeter. This was a distinct advantage because of the great number of samples to be analyzed for each run. Some error may have been introduced by employing different tubes with possible variations in light characteristics of the glass. This was determined to be slight and minimized by employing tubes from a single manufactured lot. The per cent transmittance of light was read directly from the instrument meter. It was assumed that Beer's law for absorption of light by solutions was valid, i.e., that for fixed light path the logarithm of the ratio of transmitted light, I_t/I_o, is directly proportional to the concentration of coloring matter in the solution:

$$\text{Log}_e(I_t/I_o) = kC$$

where I_t/I_o = ratio of light transmitted to light generated
C = dye concentration
k = proportionality constant, based upon length of light path and absorption coefficient of solution

Subsequently, the data were expressed in terms of the ratio of dye concentration relative to the maximum dye concentration observed for each run.

The samples from the composition transient runs were analyzed for

acetone concentration by measurement of refractive index on a Bausch and Lomb Abbe 3-L type stage refractometer. A calibration curve for the particular instrument used was prepared and found to be in reasonable agreement with literature values. Due to a flattening of the calibration curve in the region of higher acetone concentrations (above 40 mol per cent), it was beneficial for analytical measurement by this method to operate in the region of lower liquid concentration. No other special technique was required for this analysis.

MATHEMATICAL DEVELOPMENT

Formulation of Tray Model

The basic equations representing behavior of holdup in unsteady state mass transfer operations follow from the laws of conservation of mass and energy in the following form:

$$\text{input} - \text{output} = \text{accumulation} \qquad 44$$

The type of equation resulting depends upon the nature of the operation, i.e., stagewise or continuous as well as mixing assumptions. For packed columns, equation 44 takes the form of a partial differential equation, while for plate columns, the form of the equation is dependent upon the mixing assumption. Assumption of perfect mixing leads to an ordinary differential-difference equation, while any assumption involving imperfect mixing conditions leads again to a partial differential equation.

Initially, consider a differential mass balance about a three-dimensional element in a distillation column. The familiar continuity equation results:

$$\frac{\partial (L + G)_b}{\partial b} + \frac{\partial (L + G)_S}{\partial S} + \frac{\partial (L + G)_z}{\partial z} = \frac{-\partial (H + h)}{\partial t} \qquad 45$$

L = liquid flow rate
G = vapor flow rate
H = liquid holdup
h = vapor holdup
t = time
z = vertical coordinate
b = lateral coordinate
S = longitudinal coordinate
x = liquid composition
y = vapor composition

By analogy a component balance may be written:

$$\frac{\partial (Lx + Gy)_b}{\partial b} + \frac{\partial (Lx + Gy)_S}{\partial S} + \frac{\partial (Lx + Gy)}{\partial z} = \frac{-\partial (Hx+hy)}{\partial t} \qquad 46$$

For a plate column we may assume longitudinal liquid flow only and vertical vapor flow only or:

$$L_b = L_z = 0 \quad ; \quad G_b = G_S = 0 \qquad 47$$

Thus, equation 46 reduces to:

$$\frac{\partial (Lx)_S}{\partial S} + \frac{\partial (Gy)_z}{\partial z} = \frac{-\partial (Hx + hy)}{\partial t} \qquad 48$$

The type of equation which results from equation 48 above depends on the simplifying assumptions employed for characterizing the mixing.

Perfect mixing model

Assuming uniform composition across the plate, which is a result of complete, or perfect, mixing of both liquid and vapor leads to the ordinary differential difference equation:

$$(L_{j-1} X_{j-1} + G_{j-1} y_{j-1}) - (L_j X_j + G_j y_j) = \frac{d(H_j x_j + h_j y_j)}{dt} \qquad 49$$

By applying the following additional assumptions:

1. negligible vapor holdup
2. constant molar liquid holdup
3. constant molar liquid and vapor flow rates
4. adiabatic conditions

equation 49 reduces to:

$$H \frac{dx_j}{dt} = L x_{j-1} + G y_{j-1} - L x_j - G y_j \qquad 50$$

Lamb et al. (57) have shown the feasibility of a procedure involving a pseudo-equilibrium curve, which was drawn with vapor compositions equal to the true equilibrium vapor composition, y^*, multiplied by the Murphree vapor plate efficiency, E_{MV}. Therefore, further reduction may be made based on the following assumptions:

1. constant, but not necessarily equal, tray efficiencies
2. linear, but not necessarily equal, equilibrium relationship
3. small upsets can be approximated by linearized equations

Therefore, for plate j we have:

$$y_j = K_j x_j = (E_{MV})_j y_j^* = (E_{MV}\ K^*)_j\ x_j \qquad 51$$

E_{MV} = Murphree vapor plate efficiency
K^* = true vapor liquid equilibrium ratio
y^* = equilibrium vapor composition
K = slope of chord connection initial and final steady state conditions

Substituting for y_j and y_{j-1}:

$$H \frac{dx_j}{dt} = x_{j+1} + G(K_{j-1}x_{j-1}) - Lx_j - G(K_j x_j) \qquad 52$$

For total reflux conditions, i.e., L = V, and by introducing a dimensional time, θ, the equation is further simplified to:

$$\frac{dx_j}{dt} = w_{j+1} - (1+K_j)x_j + K_{j-1}\ x_{j-1} \qquad 53$$

where $$\theta = \frac{t}{(H/L)} = \frac{t}{t_{avg.}} = \frac{t}{\bar{t}} \qquad 54$$

The above result, equation 53, represents the form for each plate of a distillation column for a perfect mixing model.

Plug flow model

Beginning with equation 48, a distributed parameter model may be developed by assumption of perfect mixing of vapor leaving each tray. The following equation results:

$$\frac{\partial(H_j x_j + h_j y_j)}{\partial t} = -L_j \left(\frac{\partial x_j}{\partial S}\right)S_o + G_{j-1}\ y_{j-1} - G_j y_j \qquad 55$$

where S_o = overall active tray length

By applying the simplifying assumptions employed in the previous model development, but with the assumption of liquid in plug flow, the following partial-differential equation is obtained:

$$\frac{H}{S_o}\left(\frac{\partial x_j}{\partial t}\right) + L\left(\frac{\partial x_j}{\partial S}\right) = \frac{G}{S_o}\,\bar{y}_{j-1} - \frac{G}{S_o}\,y_j \qquad 56$$

where $\bar{y}_{j-1}$ represents an average composition of the vapors leaving the tray below, which have been assumed to be completely mixed before entering the tray under consideration. A numerical value for $\bar{y}_{j-1}$ may be attained by multiplying an average of liquid entering and leaving the plate below by an average of the pseudo-equilibrium coefficients, K_j and K_{j-1}, as follows:

$$\bar{y}_{j-1} = \left(\frac{K_{j-1} + K_j}{2}\right)\left(\frac{x_{j-1} + x_j}{2}\right) \qquad 57$$

By letting: $y_j = K_j x_j$ 51

$$\frac{H}{S_o}\left(\frac{\partial x_j}{\partial t}\right) + L\left(\frac{\partial x_j}{\partial S}\right) + \left(\frac{GK_j}{S_o}\right)x_j = \left(\frac{G}{S_o}\right)\bar{y}_{j-1} \qquad 58$$

Introducing dimensionless time, θ, as before and a fractional tray distance, w, further simplification yields for conditions of total reflux:

$$\frac{\partial x_j}{\partial \theta} + \frac{\partial x_j}{\partial w} + K_j x_j = \bar{y}_{j-1} \qquad 59$$

where $w = \frac{S}{S_o}$ 60

and $\theta = \frac{t}{(H/L)}$ 54

The above result, equation 59, is again a representative form of the equation for each plate of a distillation column for a plug flow model.

Plug flow with axial diffusion model

Assuming plug flow, but allowing for longitudinal diffusion of liquid across the tray, a material balance over a differential length of liquid path yields a partial differential equation similar to equation 54, but which includes a term with an eddy diffusion coefficient, D_E, as follows:

$$\frac{\partial (H_j x_j + h_j y_j)}{\partial t} = D_E\left(\frac{\partial^2 x_j}{\partial S^2}\right)\rho_f' S_o - L_j\left(\frac{\partial x_j}{\partial S}\right)S_o + G_{j-1}\, y_{j-1} - G_j y_j \qquad 61$$

Applying the simplifying assumptions as outlined earlier, the following partial differential equation is obtained:

$$\left(\frac{H}{S_o}\right)\left(\frac{\partial x_j}{\partial t}\right) + V_f\left(\frac{\partial x_j}{\partial S}\right) - D_E\left(\frac{\partial^2 x_j}{\partial S^2}\right) = (G_{j-1}\,\bar{y}_{j-1} - G_j y_j)/S_o \qquad 62$$

The above, equation 62, is then a one-dimension unsteady state diffusion equation, with $\bar{y}_{j-1}$ defined earlier by equation 57.

Imposing conditions of total reflux and by further substitutions for y_j, t and S; according to equations 51, 54, and 60, the simplified results are:

$$\left(\frac{\partial x_j}{\partial \theta}\right) + \left(\frac{\partial x_j}{\partial w}\right) - \left(\frac{D_E}{V_f S_o}\right)\left(\frac{\partial^2 x_j}{\partial w^2}\right) + K_j x_j = \bar{y}_{j-1} \qquad 63$$

The equation shown above represents unsteady state behavior of a plate upon which plug flow occurs with liquid diffusion in the longitudinal direction. It has been noted previously, that the coefficient of the second partial derivative with respect to w is the inverse of the Peclet number, N_{Pe}.

Perfectly-mixed pool concept model

The assumption of a tray divided into several discrete stages, each of which is completely mixed, provides a method of accounting for imperfect mixing of liquid on an overall tray. The mathematical equations may be

developed from a component balance about each of these stages. Equation 49, which is the general form of the equation for a perfectly mixed tray may be modified to represent a single perfectly mixed stage, as follows:

$$(L_{i-1}\, x_{i-1} + G_{j-1}\, x_{j-1}) - (I_i x_i + G_i x_i) = \frac{d(H_i x_i + h_i y_i)}{dt} \qquad 64$$

where i = stage number (on plate j)
j = plate number

To reduce the equation, the following simplifying assumptions are applied:

1. There are N stages per plate, each with liquid uniformly mixed.
2. Molar liquid plate holdup is constant and is equally divided among N stages, i.e., $H_K = (H_j/J) = H/N$.
3. Vapor holdup is negligible for each stage.
4. Vapor leaving each plate is uniformly mixed and vapor flow is distributed equally among N stages per plate.
5. Vapor and liquid molar flow rates are time-invariant and unchanged by flow through each stage.
6. Local efficiencies are constant for each stage but not necessarily equal.
7. Vapor-liquid equilibrium relationship is linear for each stage, but not necessarily equal.
8. Small upsets can be approximated by linearized equations.

The following equation is then obtained:

$$Lx_{i-1} - (L + \frac{G}{N} K_i)x_i + \frac{G}{N} \bar{y}_{j-1} = \frac{H}{N} \frac{dx_i}{dt} \qquad 65$$

where the inlet vapor concentration $\bar{y}_{j-1}$ is obtained as a product of an average of the pseudo-equilibrium constants for each of the stages on the plate below multiplied by an average of the compositions of each of the

stages on the plate below. That is:

$$\bar{y}_{j-1} = \left[\frac{\sum_{i=1}^{N} (K_i)_{j-1}}{N}\right] \left[\frac{\sum_{i=1}^{N} (x_i)_{j-1}}{N}\right] \qquad 66$$

Then by imposing conditions of total reflux and by introducing a dimensionless time, θ_N, based on average holdup time for each stage:

$$\theta_N = \frac{t}{(H/NL)} \qquad 67$$

equation 65 is reduced to:

$$\frac{dx_i}{d\theta_N} + (1 + K_i)x_i = x_{i-1} + \bar{y}_{j-1} \qquad 68$$

with $\quad x_j\Big|_{i=0} = x_{j+1}$

and $\quad x_j\Big|_{i=N} = x_j$

The above equation then represents unsteady state behavior of a single perfectly mixed stage on a distillation tray. The overall tray behavior may then be resolved by employing similar equations for each stage.

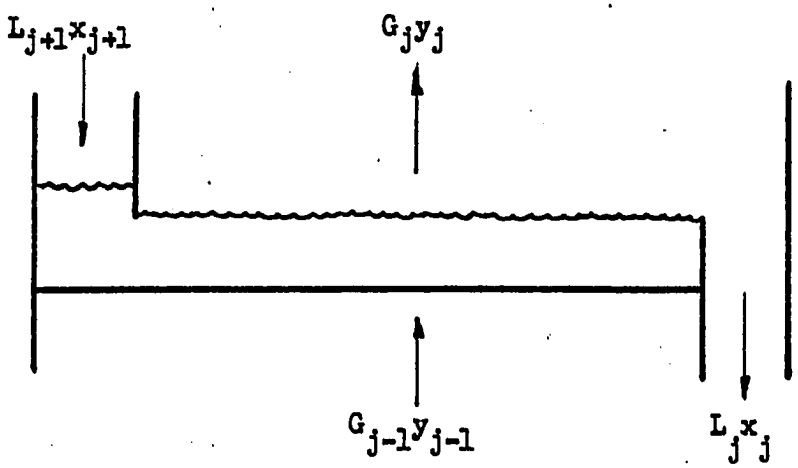
Determination of Mixing Parameters

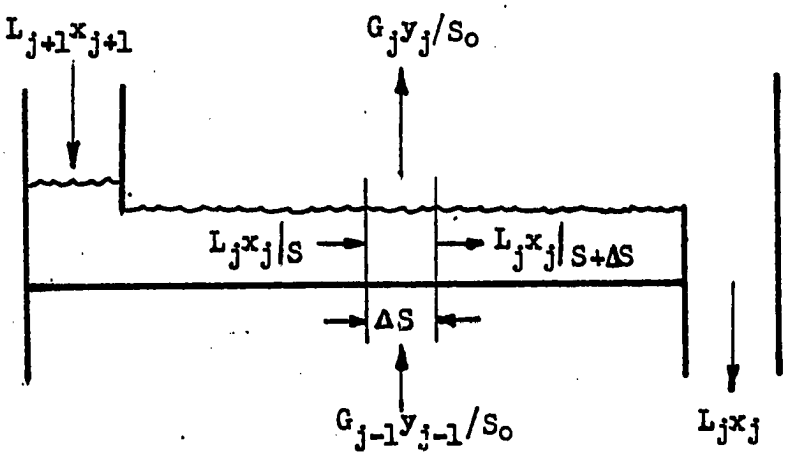
Liquid traversing a commercial distillation tray can be expected to be subject to longitudinal mixing effects. A sizable effort has been put forth to determine parameters characterizing these effects between the extreme cases of perfect mixing and plug flow. A further consideration is that the mixing parameters developed herein must be in a form adaptable to the aforementioned models describing mass transfer dynamic effects. Incomplete mixing of the liquid is reflected by the existence of a concentration gradient in the liquid phase across the tray. The result is that a range of

Fig. 10. Single stage perfect mixing model

Fig. 11. Plug flow model

Fig. 12. Multi-stage perfect mixing model


$L_{j+1}x_{j+1}$
G_jy_j
$G_{j-1}y_{j-1}$
L_jx_j


$L_{j+1}x_{j+1}$
G_jy_j/S_o
$L_jx_j|_S$
$L_jx_j|_{S+\Delta S}$
ΔS
$G_{j-1}y_{j-1}/S_o$
L_jx_j

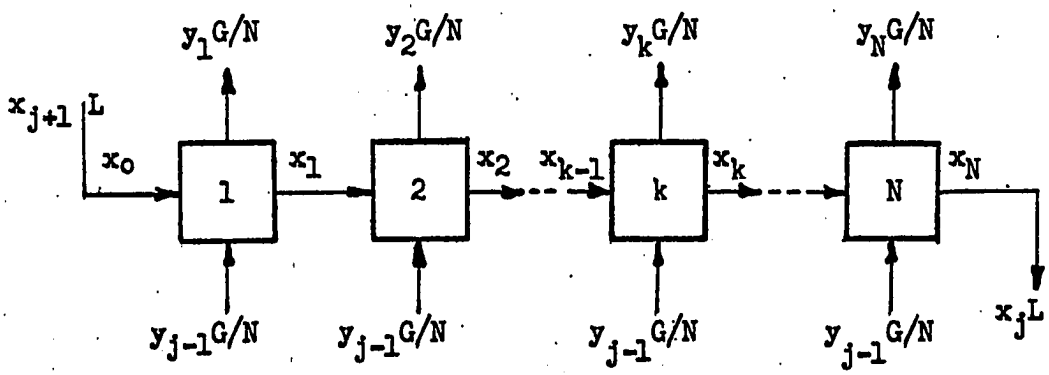
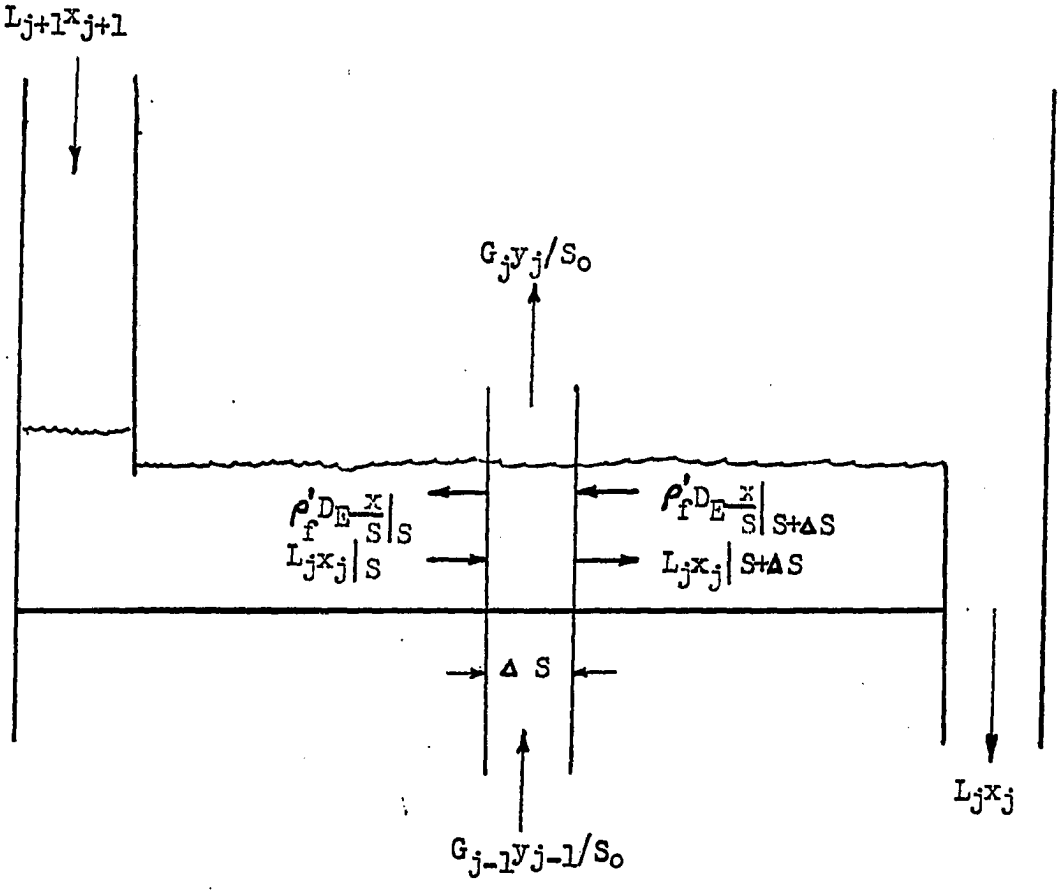

y_1G/N
y_2G/N
y_kG/N
y_NG/N
x_{j+1}
L
x_o
1
x_1
2
x_2
x_{k-1}
k
x_k
N
x_N
$y_{j-1}G/N$
$y_{j-1}G/N$
$y_{j-1}G/N$
$y_{j-1}G/N$
x_jL

Fig. 13. Plug flow with diffusion model


$L_{j+1}x_{j+1}$
G_jy_j/S_o
$\rho'_f D_E \frac{x}{S}\Big|_S$
$L_jx_j|_S$
$\rho'_f D_E \frac{x}{S}\Big|_{S+\Delta S}$
$L_jx_j|_{S+\Delta S}$
ΔS
L_jx_j
$G_{j-1}y_{j-1}/S_o$

tray residence times is possible for an entering volume of liquid. Experimental residence time distribution functions (rtdf) afforded the greatest possibility for achievement of an all-inclusive set of mixing parameters. The alternatives consisted chiefly of empirical correlations, which were for the most part, quite limited in their application. By comparison, the residence-time concept is quite descriptive of the mixing characteristics whatever their nature. A further important distinction of residence time analysis is that the fundamental statistical probability theory can be brought to focus upon the experimental results because of the mathematical similarities.

The cumulative residence time function, F(t), describes the fraction of liquid particles having residence time of t or less. This is consistent with a cumulative probability function. The residence time distribution function, (rtdf) describes the frequency or probability density function, f(t), and is related to the cumulative function by:

$$f(t) = \frac{d\,F(t)}{dt} \qquad 69$$

where $$\int_0^\infty f(t)dt = 1 \qquad 70$$

F(t) is non-decreasing; F(0) = 0; F(∞) = 1

The rtdf, therefore, may be employed with differential time as f(t)dt, which describes the probability of a residence time between t and (t + dt).

The residence time distribution function can be determined experimentally as the system response to an impulse function, imposed as an input disturbance to the system in the form of a tracer. Similarly, the experimental system response to a step-change as the input disturbance to the system, determines the cumulative distribution function, F(t). Several

different responses to each of these input responses are possible based upon different mixing characteristics (see figs. 14, 15). From these two functions, a wide range of functions of various types may be developed. Of prime importance among these are the moments of the distribution function, whose general formula for the r^{th} moment about the origin is given as:

$$\mu'_r = E(t^r) = \int_0^\infty t^r f(t)dt \qquad 71$$

The general formula for the r^{th} moment of a distribution function about the mean is:

$$\mu_r = E\left\{\left[t-E(t)\right]^r\right\} = \int_0^\infty \left[t-E(t)\right]^r f(t)dt \qquad 72$$

In the event calculation of the higher moments becomes tedious, an alternate method for evaluation is based upon the moment generating function defined as:

$$E(e^{\mu t}) = \int_0^\infty e^{\mu t} f(t)dt \qquad 73$$

which is noted to be the definition of the Laplace transform. The r^{th} moment about the origin may then be computed from:

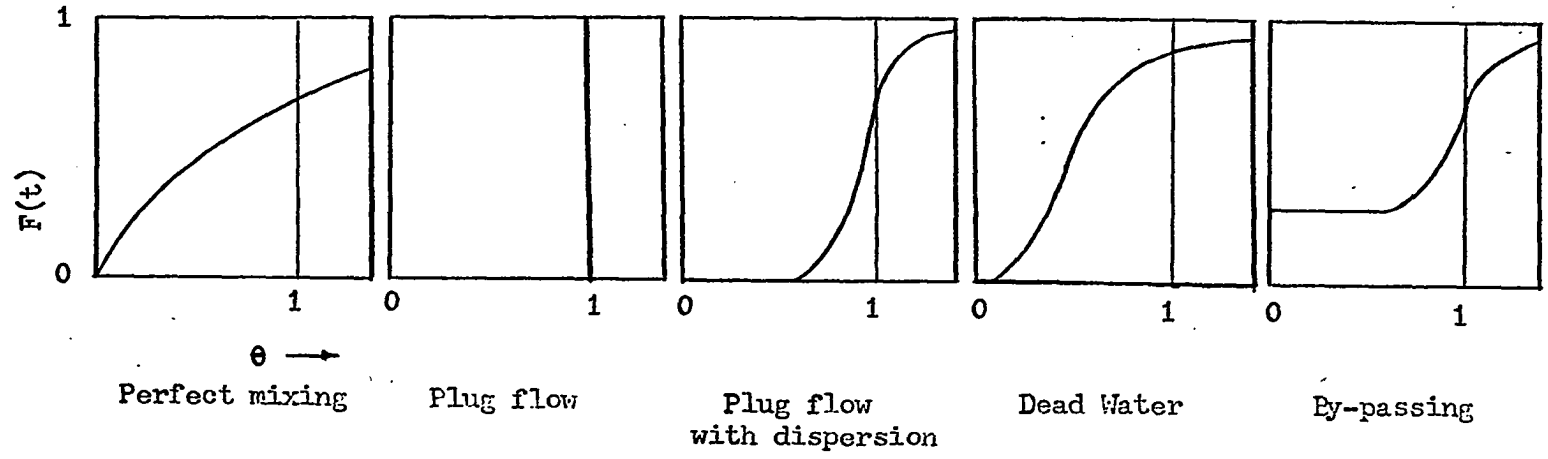
$$\mu'_r = \frac{d^r\left[E(e^{\mu t})\right]}{dt^r} \quad \text{evaluated at } t=0 \qquad 74$$

The importance here rests on the ability to express the rtdf as an analytical function, which can be transformed. Conversely, if the moment generating function is known, the rtdf is uniquely determined. The exact number of moments needed to uniquely determine the rtdf is not readily foreseen. Nevertheless, the statistical moments do bear considerable significance.

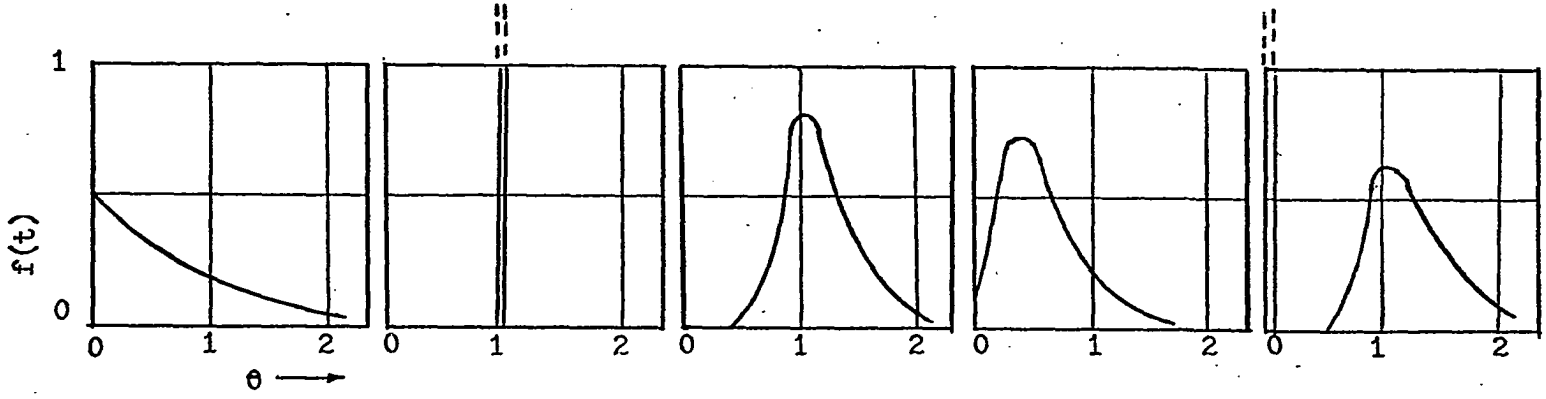
The first moment about the origin, μ'_1, describes the average or, statistically, the expected value of t for the distribution function. When

Fig. 14. Typical cumulative distribution function (step response)

Fig. 15. Typical residence time distribution function



Perfect mixing | Plug flow | Plug flow with dispersion | Dead Water | By-passing



Perfect mixing | Plug flow | Plug flow with dispersion | Dead Water | By-passing

f(t) represents a residence time distribution, the expected value, E(t), is the mean residence time or average age of a particle in the system studied.

$$\bar{t} = \mu_1' = E(t) = \int_0^\infty t f(t)dt \qquad 75$$

The second moment about the mean, μ_2, signifies the variance, or dispersion about the mean, of the distribution function, Consequently, the variance of an rtdf characterizes the dispersion of residence times.

$$\sigma^2 = \mu_2 = E\left\{[t-E(t)]^2\right\} = \int_0^\infty [t-E(t)]^2 f(t)dt \qquad 76$$

$$\sigma^2 = E(t^2) - E^2(t) = \mu_2' - (\mu_1')^2 \qquad 77$$

$$\text{where } \mu_2' = \int_0^\infty t^2 f(t)dt \qquad 78$$

The coefficient of variation is employed to express the dispersion relative to the mean of the distribution.

$$\gamma(t) = \frac{\sqrt{\sigma^2}}{\bar{t}} = \frac{\sqrt{\mu^2}}{(\mu_1')} \qquad 79$$

Subsequently, a further significance will be attached to the variance and coefficient of variation.

The third moment with respect to the mean, μ_3, is employed in a statistical parameter, α_3, which is a measure of the skewness or asymmetry of a distribution about its mean.

$$\alpha_3 = \frac{E\{[t-E(t)]^3\}}{\sigma^3} = \frac{\mu_3}{(\mu_2)^{3/2}} \qquad 80$$

$$\text{and } \mu_3 = \mu_3' - 3\mu_1'\mu_2' + 2(\mu_1')^3 \qquad 81$$

$$\text{where } \mu_3' = \int_0^\infty t^3 f(t)dt \qquad 82$$

It may be noted that among the first four moments, only the third can be either positive or negative, depending upon whether the distribution is skew right or left. Correspondingly, the skewness parameter, α_3, is

zero for a symmetric distribution.

A statistical parameter, α_4, based upon the fourth moment about the mean, μ_4, describes the peakedness of the distribution function, referred to as kurtosis.

$$\alpha_4 = \frac{E\{[t-E(t)]^4\}}{\sigma^4} = \frac{\mu_4}{(\mu_2)^2} \qquad 83$$

$$\text{and } \mu_4 = \mu_4' - 4\mu_1'\mu_3' + 6(\mu_1')^2\mu_2' - 3(\mu_1')^4 \qquad 84$$

$$\text{where } \mu_4' = \int_0^\infty t^4 f(t)dt \qquad 85$$

All of the composition transient models presented in a previous section required substitution of a mean residence time for solution. The value of determining the average residence time from the experimental mixing response is realized from difficulty in obtaining an accurate direct measurement of residence time on an operating distillation tray. Further, the effects of by-passing, dead space, time delay or back-mixing are accounted for.

The eddy-diffusion approach to a tray model, as discussed earlier, has been employed in a number of previous efforts to describe liquid mixing. The basic liquid mixing parameter involved is the dimensionless Peclet number, which has been described as being similar to the number of perfectly mixed pools in the pool concept model. Van der Laan (104) presented solutions of the diffusion equation in terms of the variance of the distribution function which he related generally as:

$$\sigma^2 = \left(\frac{2}{N_{Pe}^2}\right)\left(N_{Pe} - 1 + e^{-N_{Pe}}\right) \qquad 86$$

$$\text{where } N_{Pe} = \frac{V_f S}{D_E} \qquad 87$$

V_f = froth velocity, ft/sec
S = tray distance, ft
D_E = eddy diffusion coefficient, ft/sec

Foss (31) observed that the variance was a function of the eddy-diffusion coefficient, tray length and mean froth velocity:

$$\sigma^2 = \sigma^2 \bar{t}^2 = \frac{1}{V_f}\left(\frac{2D}{V_f^2}\right)S = \left(\frac{2D_E}{V_f S}\right)\bar{t}^2 = \left(\frac{2}{N_{Pe}}\right)\bar{t}^2; \text{ for } \frac{1}{N_{Pe}} < 1 \qquad 88$$

This is recognized as a special case of the relationship of Van der Laan. Subsequently, it was shown by Foss that differentiating his previous expression resulted in the following expression relating the rate of increase of the variance with tray distance:

$$\frac{d\hat{\sigma}^2}{dS} = \frac{2D_E}{V_f^3} \qquad 89$$

The equation predicts, for a constant eddy-diffusivity and froth velocity, that a linear increase of variance results. Thus where prescribed diffusion conditions hold, the eddy diffusion coefficient may be determined from the slope of the variance-tray distance relationship. It must be noted by comparison of the expressions of Van der Laan and Foss that the above slope determination technique for the diffusion coefficient is an approximation. Levenspiel (60), however, has shown the error of the approximation to be slight for sufficiently large values of the Peclet number. A similarity is observed here between the relationship of Foss and the coefficient of variation, γ. Where the tray distance is directly proportional to residence time as a particle progresses through the system, the variance relationship is observed to be linear from the initial point:

$$\frac{d\hat{\sigma}^2}{d\,S_o} = \frac{2D_E}{V_f^3} = \frac{\hat{\sigma}^2}{\bar{t}} = \gamma^2\bar{t} \qquad 90$$

The third moment of the distribution function, as discussed earlier, describes skewness and might therefore be considered a measure of the approach of the system to perfect mixing. Similarly, the fourth moment, measuring peakedness, might be considered a measure of the approach to plug flow. Beyond comparison of these moments for various distribution functions, they were not encompassed in a particular tray mixing model.

Other techniques employing rtdf are available, such as the concepts of "holdback" and "segregation," as presented by Danckwerts (25), both of which provide a measure of deviation from perfect mixing. It is evident that a great deal of information is available from residence time functions and that various analysis techniques are available. While many of these techniques may provide valuable insight, incorporation of the results into a linearized tray model in parametric form is not always a direct possibility.

DISCUSSION OF RESULTS

The experimental results can be separated into two distinct categories, first, measurement of liquid mixing effects at steady state mass transfer conditions, and second, measurement of transient response to changes in composition. Liquid mixing was studied by injection of a non-volatile dye tracer at the inlet and observing the dispersion by measuring changes in dye concentration with time at several points along the tray simultaneously. The response to a stepwise disturbance in the inlet liquid composition was similarly observed at several points along the length of the tray.

During the theoretical phase of the work, analog computation was used extensively. Initially, the experimental mixing results were simulated to permit analytical evaluation of the moments of the distribution functions. The mixing parameters thus derived were incorporated into mathematical models to describe both the mixing and mass transfer operations as they occur on the tray during the unsteady state. Several such distributed parameter models were evaluated along with a lumped parameter model for their ability to predict the transient composition response.

Liquid Mixing

Experimental

The acquisition of accurate experimental data concerning liquid mixing conditions was an important phase of the project. There were two levels of mixing investigated, corresponding to different liquid flow rates at initial steady state conditions. Mixing characteristics of a distillation tray are primarily governed by tray design, therefore

adjustment of operating conditions (e.g. liquid flow rate) alters the mixing over a limited range only. This is not to indicate that study of effects of changing other facets of column operation (e.g. outlet weir height) would not provide valuable information. The results obtained at the two levels of liquid rate employed, however, represent quite well the mixing characteristics of the specific tray design employed. This data was intended to enable development of models for predicting transient composition response, therefore no attempt was made to formulate empirical correlations of the effects of operating conditions upon mixing characteristics.

Visual observation of the froth on the tray indicated uniform vapor distribution, i.e. no "blowing" of the tray, with an approximate froth height of 3 inches across the tray. Liquid temperatures taken at five points across the tray were uniform. There was also only a slight difference in observed tray conditions for the two liquid flow rates studied (see figs. 16, 17, 18, 19). Higher liquid flow rates were not possible under conditions of atmospheric distillation, since at the higher boilup rates pressure was built up causing considerable acetone loss through the system vents.

The response of the tray at each axial series of five sample taps to a step change in dye concentration of the input liquid was determined simultaneously. The data were alternately gathered for the center and right side series of sample locations at each flow rate (see figs. 20, 21, 22, 23). The experimental data are collectively presented in the appendix.

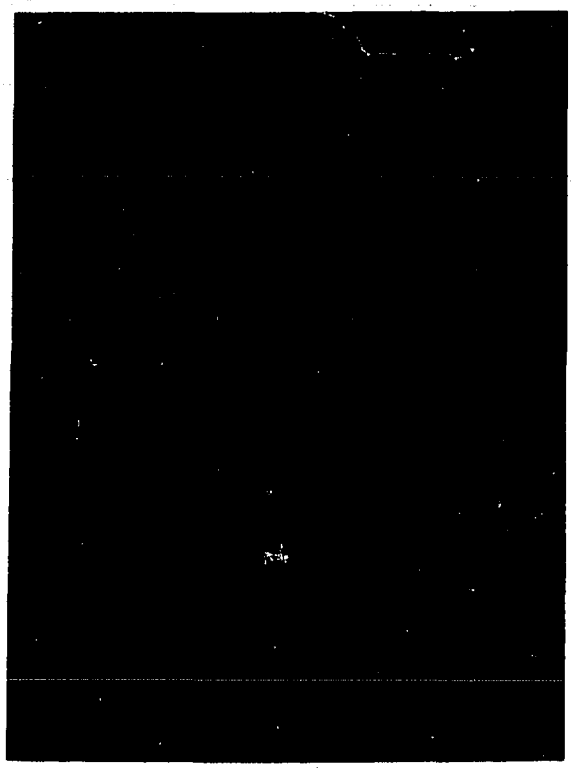
The initial examination of the response curves revealed that although the first tap in each series of sample taps was only 1 inch from the inlet

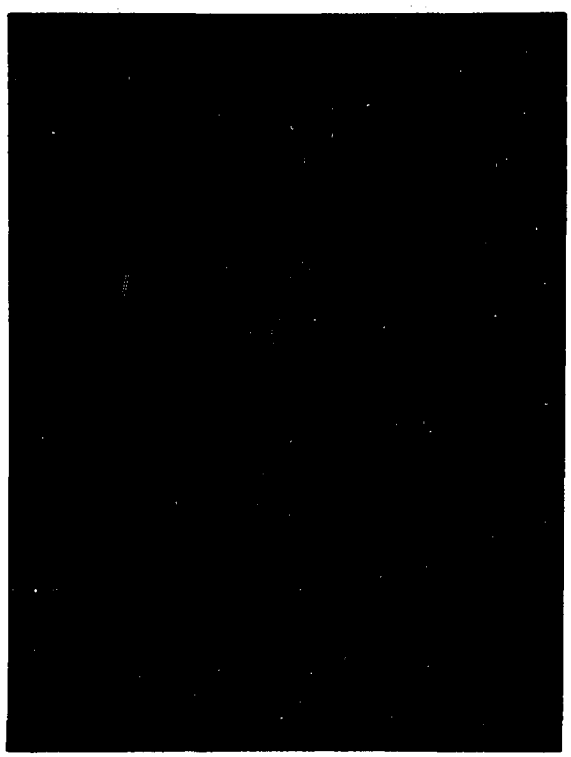
Fig. 16. Tray during operation at high liquid flow rate, 0.9 gpm (back lighted)

Fig. 17. Tray during operation at high liquid flow rate, 0.9 gpm (front lighted)

Fig. 18. Tray during operation at low liquid flow rate, 0.6 gpm (back lighted)

Fig. 19. Tray during operation at low liquid flow rate, 0.6 gpm (front lighted)





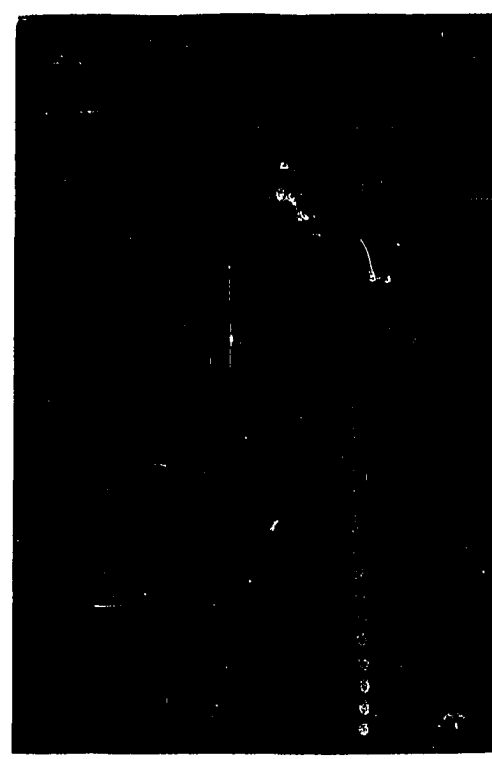


Fig. 20. Response to step-change in dye concentration at center series of sample locations with low liquid flow rate, 0.6 gpm, shown with simulated response curves

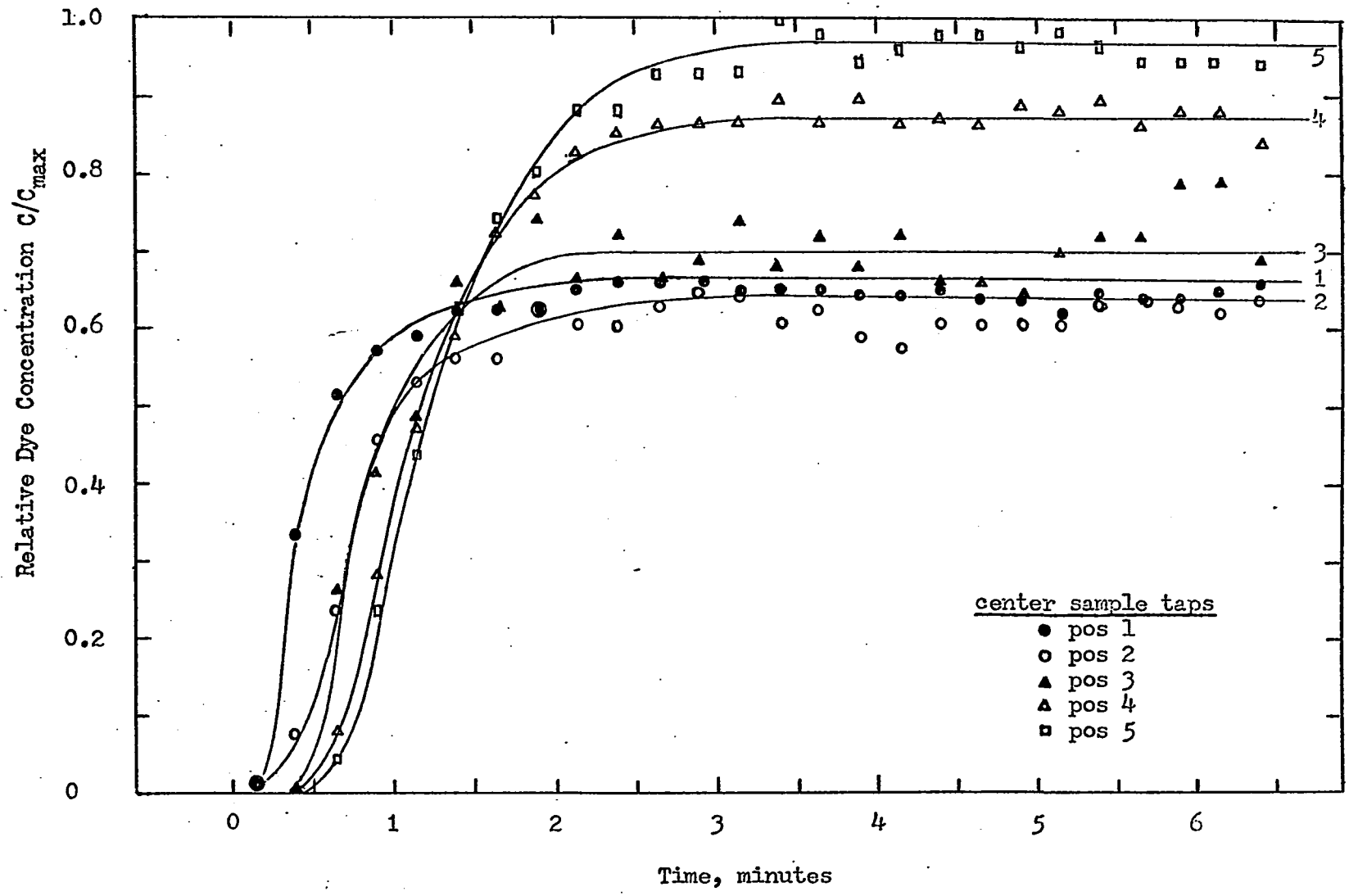

1.0
0.8
0.6
0.4
0.2
0
Relative Dye Concentration C/C max
0
1
2
3
4
5
6
Time, minutes
5
4
3
1
2
center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5

Fig. 21. Response to step-change in dye concentration at side series of sample locations with low liquid flow rate, 0.6 gpm, shown with simulated response curves.

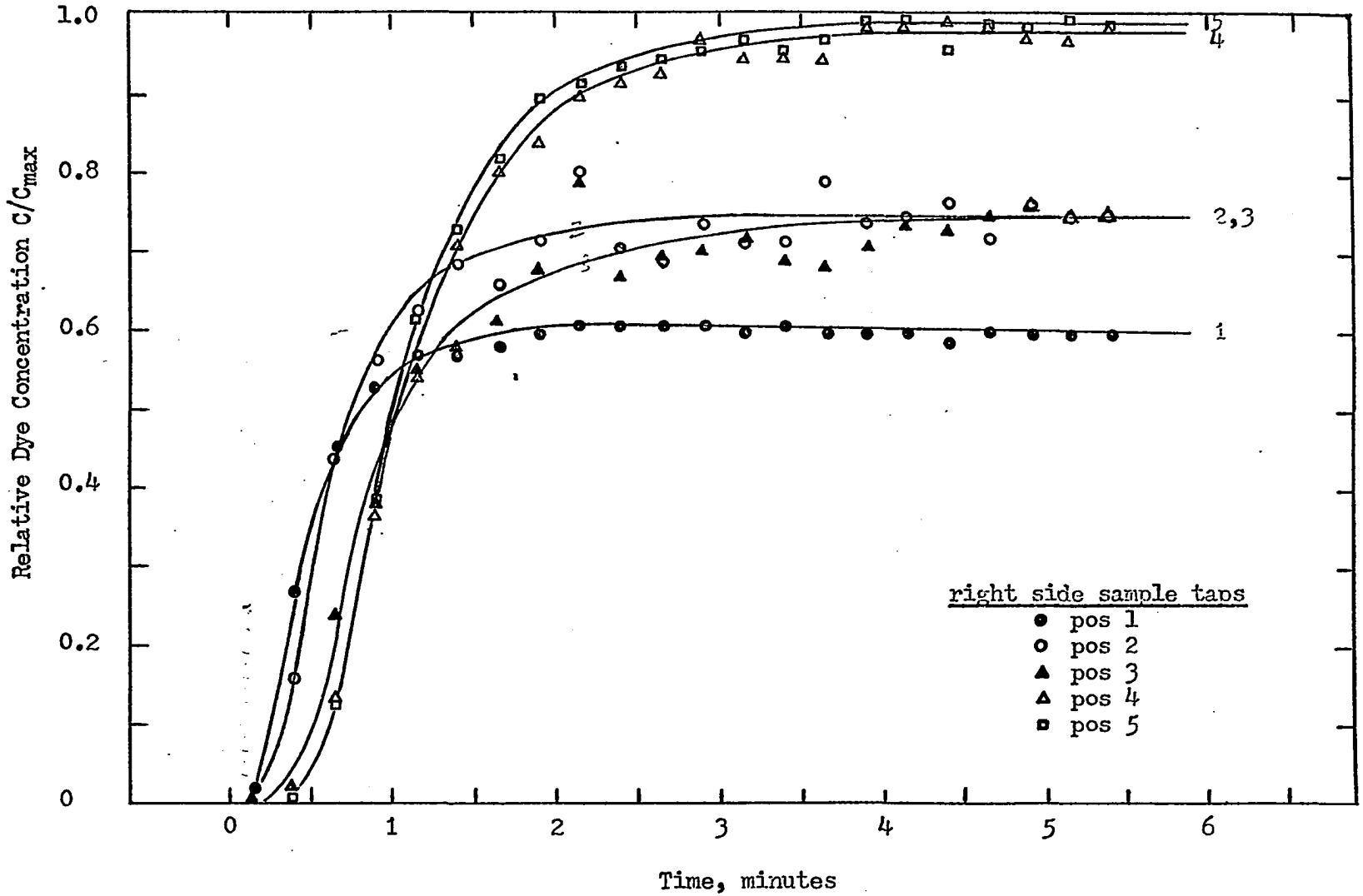

1.0
0.8
0.6
0.4
0.2
0
Relative Dye Concentration C/Cmax
0
1
2
3
4
5
6
Time, minutes
5
4
2,3
1
right side sample taps
pos 1
pos 2
pos 3
pos 4
pos 5

Fig. 22. Response to step-change in dye concentration at center series of sample locations with high liquid flow rate, 0.9 gpm, shown with simulated response curves

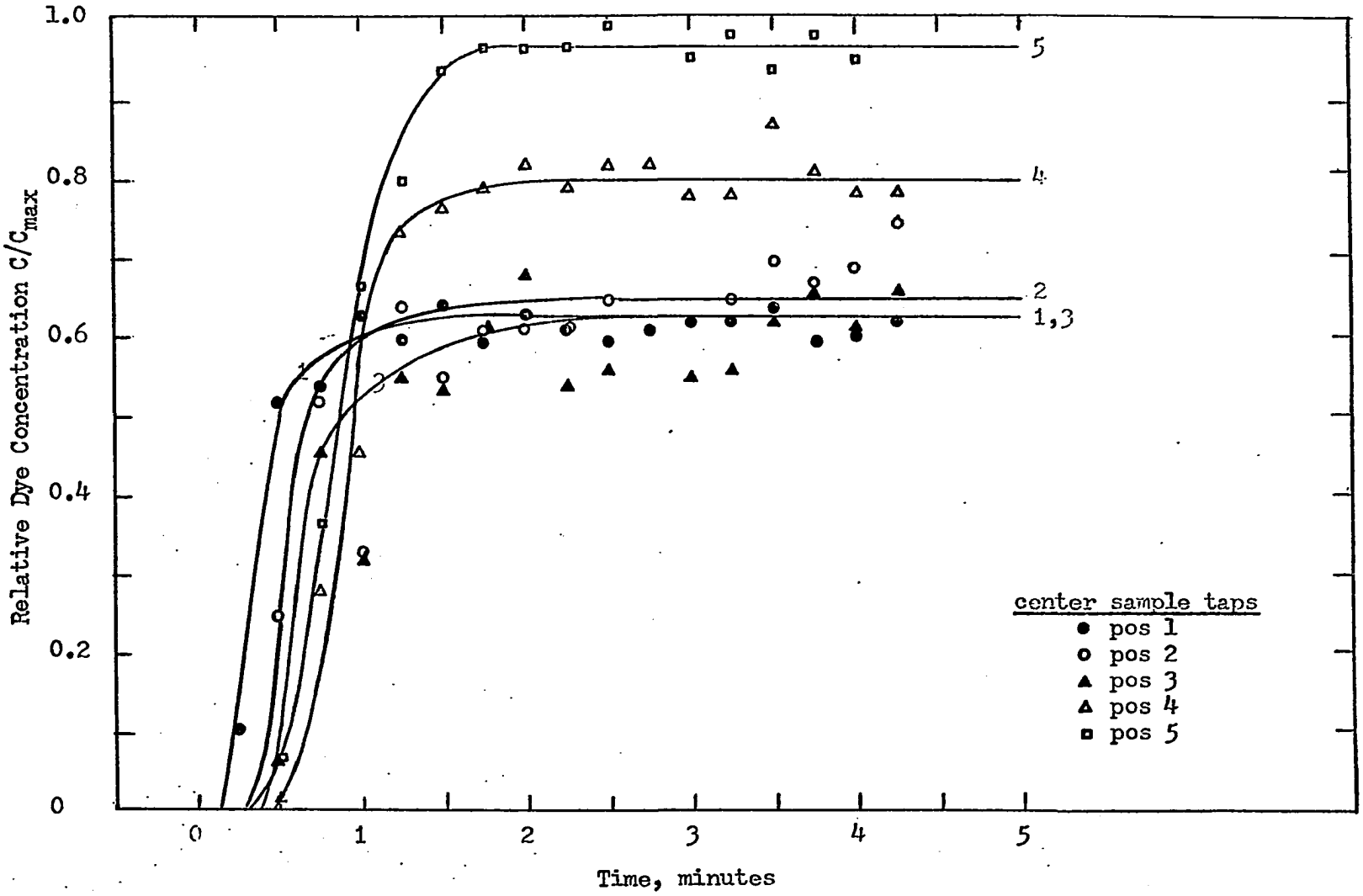
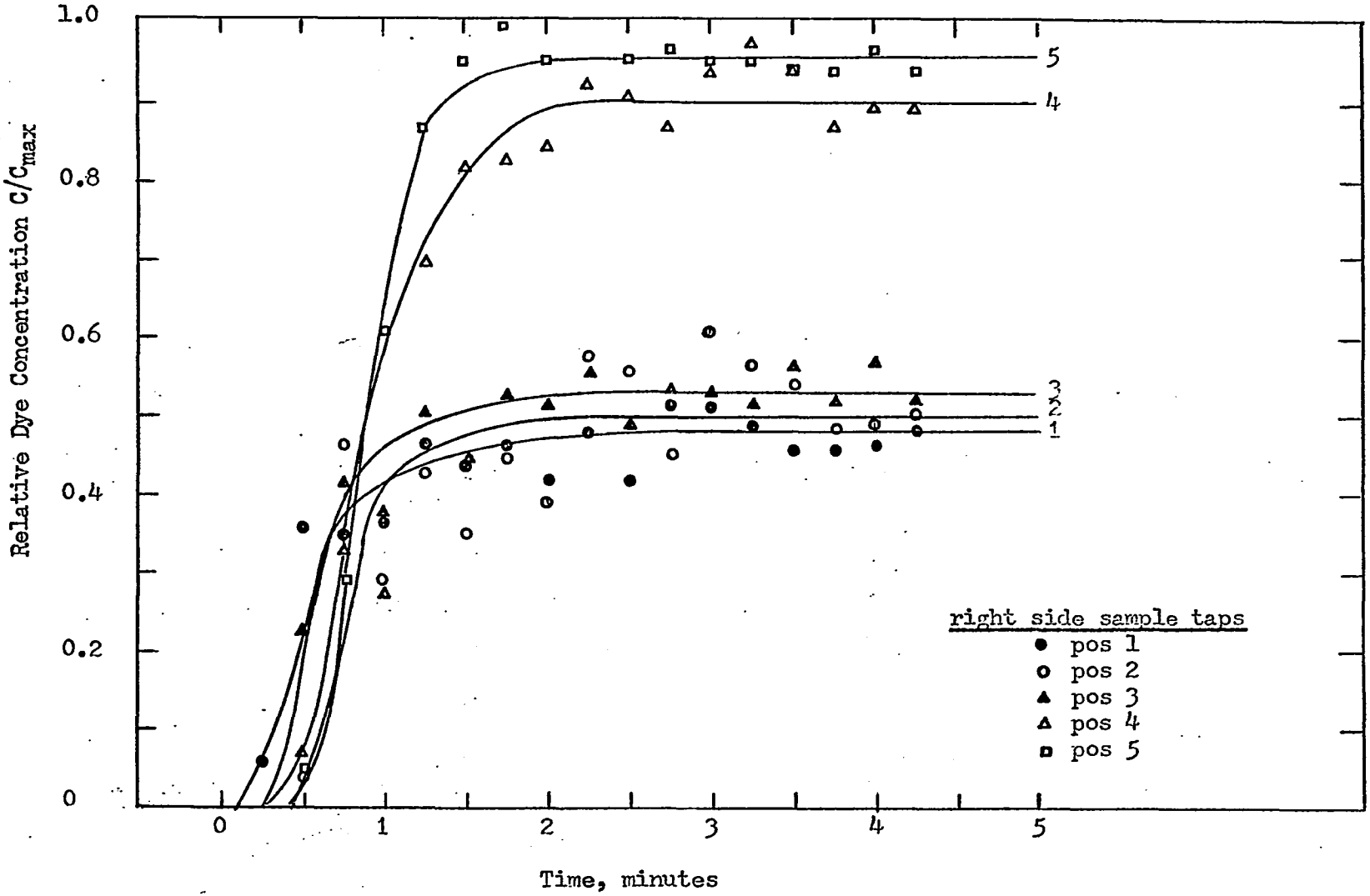

1.0
0.8
0.6
0.4
0.2
0
Relative Dye Concentration C/C max
0
1
2
3
4
5
Time, minutes
5
4
2
1,3
center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5

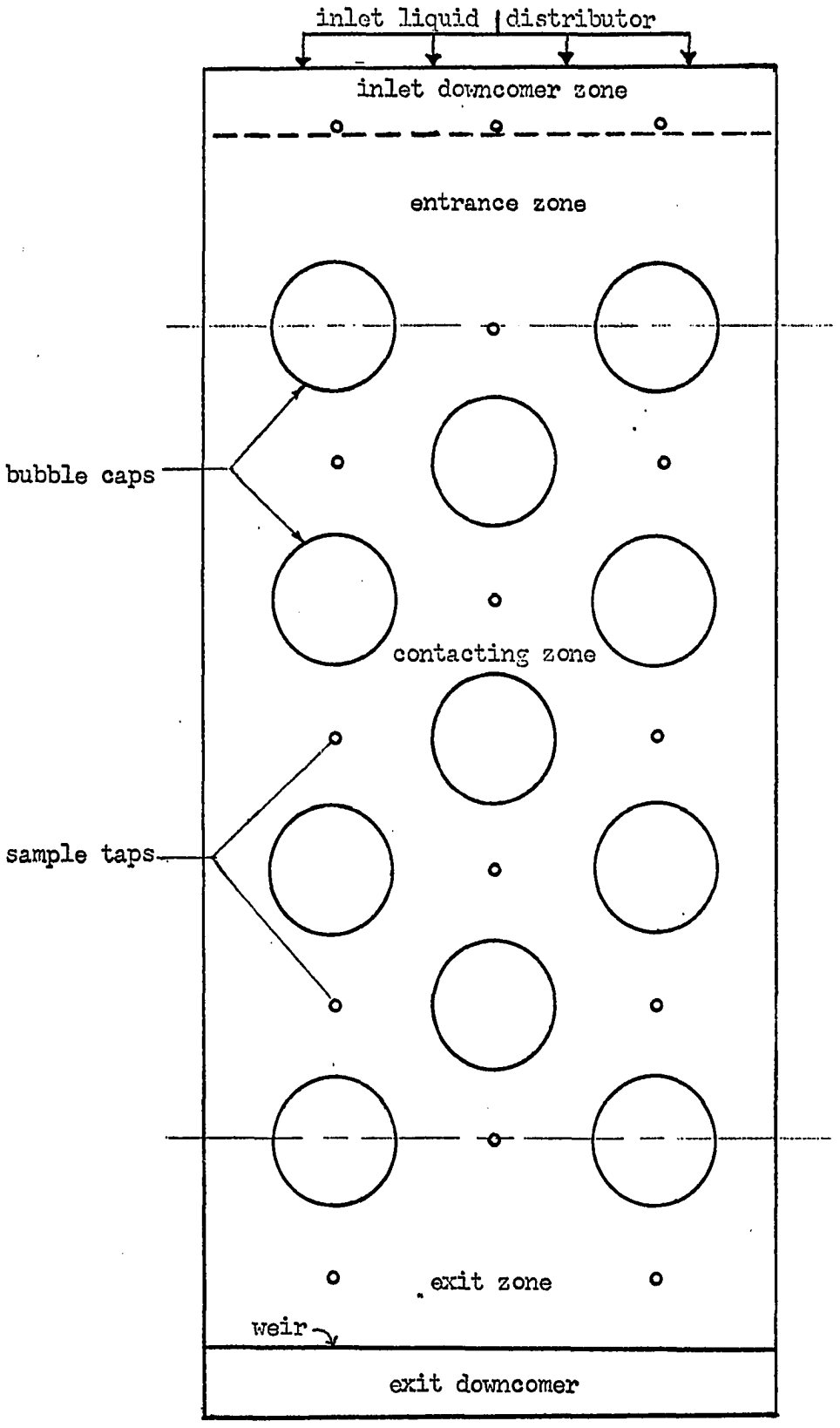
Fig. 23. Response to step-change in dye concentration at side series of sample locations with high liquid flow rate, 0.9 gpm, shown with simulated response curves


1.0
0.8
0.6
0.4
0.2
0
Relative Dye Concentration C/Cmax
0
1
2
3
4
5
Time, minutes
5
4
3
2
1
right side sample taps
pos 1
pos 2
pos 3
pos 4
pos 5

wall, considerable liquid mixing had occurred. This mixing lag, as opposed to a pure time delay, must be attributed to the inlet downcomer design. The liquid entry system was specifically constructed to be similar to an actual tray feed system, with liquid allowed to enter the side of the column and drain to the tray below. Extension of the liquid inlet piping through the column wall to a point beneath the tray liquid level might have reduced the mixing prior to the first sample point, but the gravity-fed reflux system might also have required revision. The problem, however, of mathematical treatment of this downcomer mixing lag is a quite realistic one, encountered in simulation of commercial trays. Previous discussion concerned literature references (104, 108) which further involved the division of process equipment into several zones, e.g. entrance, contacting and exit zones. Therefore, the experimental tray might well be considered in four sections: downcomer, entrance, contacting and exit zones (see fig. 24). The downcomer zone is obviously the area from the point of liquid entry at the column wall to the first sample tap. The entrance zone may be considered to extend from the first sample tap to the second sample tap on the center axis, which corresponds to the first row of bubble caps. The contacting zone is the area between the first and last rows of caps, which corresponds to the area between second and fifth center sample taps respectively. The exit zone extends from the last row of caps to the outlet weir. The significance of the breakdown is based upon a consideration of the different mixing conditions for each section, the analysis of which will be discussed later.

The time element concerning the introduction of the upset to the column and withdrawal of samples must also be considered. Each point as shown on

Fig. 24. Experimental tray layout showing mathematical division


inlet liquid distributor
inlet downcomer zone
entrance zone
bubble caps
contacting zone
sample taps
exit zone
weir
exit downcomer

the mixing response curve represents an average composition for a 12 second interval, allowing an additional 3 seconds for rotation of the fraction collector table to the next set of test tubes. The sample lines were considered to introduce only time delay, which was assumed equal for all lines, and was experimentally determined to be less than 6 seconds for each. The sample lines apparently were filled with a vapor-liquid mixture before the cooler section, thereby reducing the time delay below that expected for a line completely filled with liquid. Due to slight positive pressure in the column, no difficulty was experienced in removing samples from the column. The time required for the upset to reach the column wall following introduction at the control panel valves was calculated to be 12.5 seconds at the high liquid rate of 0.9 gpm and 19 seconds at the low liquid rate of 0.6 gpm. In curves representing mixing data or response curves (see figs. 20, 21, 22, 23) time zero is the estimated time the upset reached the column wall. Sample line delay is therefore included in response time.

Simulation

The determination of mixing parameters from the results of the experimental mixing response curves was accomplished with the aid of an Electronic Associates Model TR-48 analog computer.

The mixing response curves resulting from the step-change in dye concentration represent the cumulative, or F-distribution function. The residence time distribution function, or rtdf, however is given by the response to an impulse. Since pulse testing was not attempted for this project the rtdf must be determined from the derivative of the F-distribution, as

discussed previously.

The initial attempt to determine the rtdf employed a curve-follower device, which served to generate the cumulative distribution function as an input to an approximate derivative routine on the analog computer. The actual derivative is accomplished on the computer by patching a capacitor into the summing junction of an operational amplifier with a feedback resistor (see fig. 25). The approximate derivative routine employed was achieved by inserting a small resistance between the capacitor and the amplifier (see fig. 26). As shown, the input resistor must be small to avoid appreciable error. Of the routines examined this particular system was found to provide the best results. As employed, the system is effectively a low-pass filter which removes the high frequency noise which is the major objection to use of the actual derivative system.

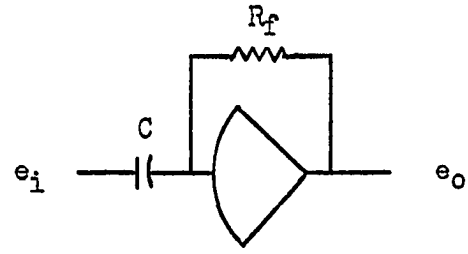
Use of the curve-follower mechanism involved plotting a smooth curve through data points. The rtdf resulting from the derivative of this input function, while acceptable, did not result in a smooth response, because of slight curve-follower fluctuation.

Determination of the distribution moments about the origin by direct integration of the appropriate functions on the analog computer resulted in excessive error for the higher moments. The difficulty was encountered due to multiplication of an extremely large quantity (e.g. x^4) by an extremely small quantity(i.e. f(t)). Although high-accuracy electronic quarter-square multipliers were employed, the difficulty was of an extreme nature.

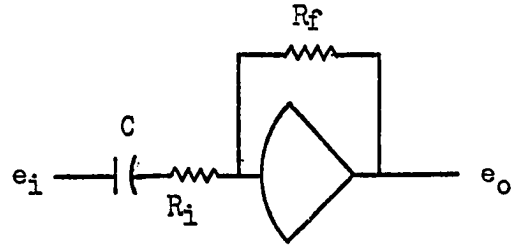
To achieve an accurate estimate of the moments of the rtdf, the alternate approach of simulating the rtdf was selected. The tray was approximated

Fig. 25. Actual derivative routine

Fig. 26. Approximate derivative routine



Transfer Function: $\frac{e_o}{e_i} = R_f C s$



Note: $R_i \cong 0.1\ R_f$

Transfer Function: $\frac{e_o}{e_i} = \frac{R_f C s}{1 + R_i C s}$

by a series of perfectly mixed stages, that is, a series of non-interacting first-order elements. The time constants for the simulated function were obtained by comparing the computer-generated rtdf with the rtdf based upon the experimental mixing results. The experimental rtdf was formed by the method described above, employing the curve-follower mechanism and the approximate derivative routine. The simulated rtdf's were smooth curves obtained by differentiating the step-change response of the simulated function by the approximate routine (see figs. 27, 28, 29, 30). The coefficient potentiometers on the analog computer were adjusted until the proper fit was attained. The final settings were representative of the time constants for the simulated function.

The primary advantage of this simulation technique is the application of Laplace transform methods to obtain the moments of the distribution function. When the cumulative distribution, or step-response, is represented by an exponential function, the rtdf and moment-generating function may be expressed analytically. This factor is a necessary condition for employing the Laplace transforms. Another important advantage of simulation is the more accurate representation of the "tail" on the step-change response, which is a result of the asymptotic approach of an exponential function to steady state. Experimental error, though within reasonable limits, makes an accurate estimate of a gradual approach to steady state a difficult task.

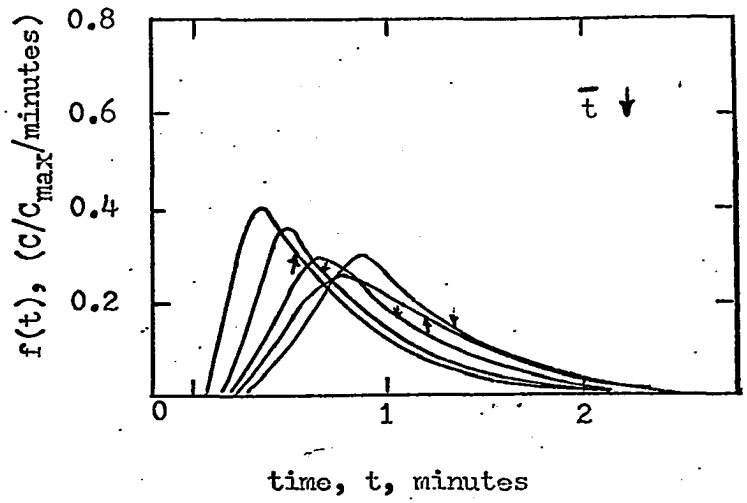
The general formula which yields the normalized mixing response for n stages of equal size, i.e. equal time constants, is given by:

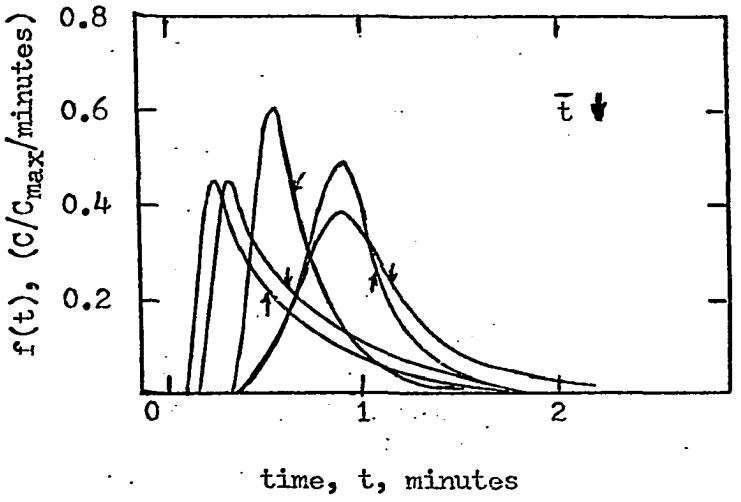
Fig. 27. Residence time distribution function, low liquid rate, 0.6 gpm, side sample locations

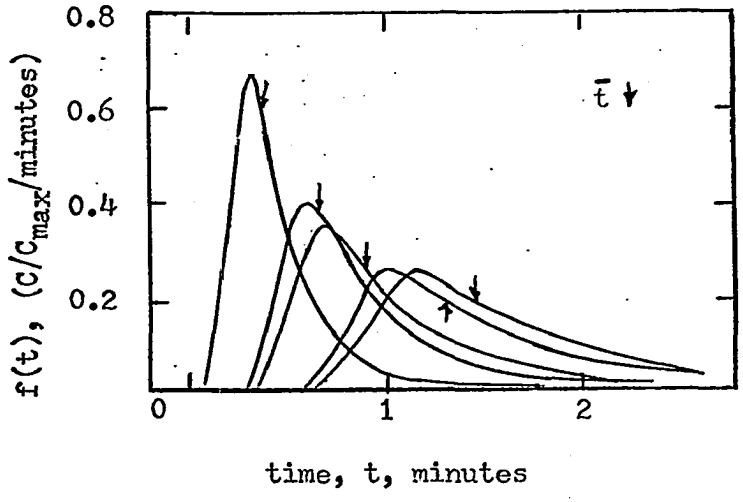
Fig. 28. Residence time distribution function, low liquid rate, 0.6 gpm, center sample locations

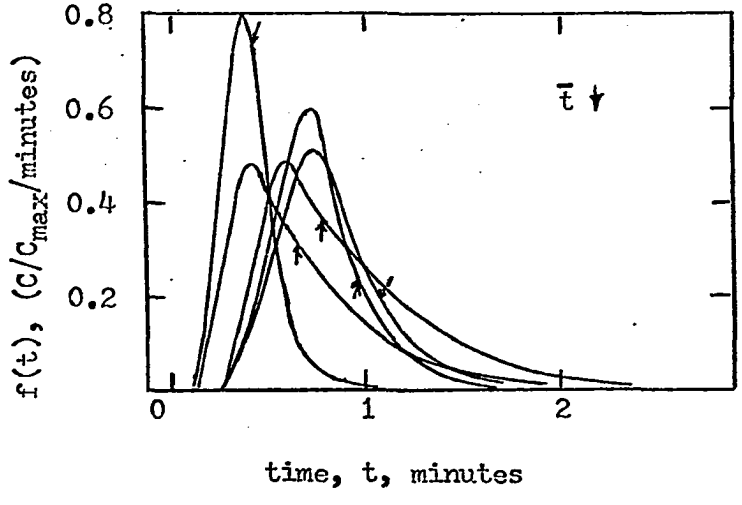
Fig. 29. Residence time distribution function, high liquid rate, 0.9 gpm, side sample locations

Fig. 30. Residence time distribution function, high liquid rate, 0.9 gpm, center sample locations


f(t), (C/C_max/minutes)
0.8
0.6
0.4
0.2
0
1
2
t̄
time, t, minutes


f(t), (C/C_max/minutes)
0.8
0.6
0.4
0.2
0
1
2
t̄
time, t, minutes


f(t), (C/C_max/minutes)
0.8
0.6
0.4
0.2
0
1
2
t̄
time, t, minutes


f(t), (C/C_max/minutes)
0.8
0.6
0.4
0.2
0
1
2
t̄
time, t, minutes

$$F(t) = x_n(t) = 1-e^{-t/T} \sum_{i=0}^{n-1} \frac{(t/T)^i}{i!} \qquad 91$$

x = composition as function of time
t = time, sec
T = time constant for each equal stage, sec
i = stage number
n = total number of stages

When there are n-1 equal stages and one additional unequal stage the overall response is: 92

$$F(t) = x_n(t) = \left[1 - \left(\frac{\phi}{\phi-T}\right)^{n-1} e^{-t/\phi} + e^{-t/T} \sum_{i=0}^{n-2}\left\{\frac{(t/T)^i}{i!} \sum_{j=0}^{n-i-2} \frac{\phi^j}{(T-\phi)^{j+1}}\right\}\right]$$

T = time constant for equal stages, sec
ϕ = time constant for unequal stage

Results of trial and error simulation by analog computer indicate that all the responses were approximated by either of the two F-functions above. The higher flow rate resulted in a 10 stage simulation function compared to a 6 stage function for the lower flow rate. Results for profiles at the center and side of the tray are in reasonable agreement, thereby indicating a somewhat uniform lateral distribution (see figs. 20, 21, 22, 23).

The simulation was generally accomplished with a series of equal stages plus one larger stage. The formulation of the exact function was largely by a trial and error procedure, though certain constraints were noted. For an example, the mean residence time, as will be shown subsequently, equals the sum of the time constants for individual elements. The residence time functions were all peaked, which aided in the fitting of the appropriate function to the curve (see figs. 27, 28, 29, 30). The single large time constant controlled the "tail" of the rtdf and largely represented

diffusion or back-mixing. This is easily comprehended from the limiting case of infinite back-mixing, or perfect mixing. The forward portion of the peak might be characterized as forward mixing, or the sharpness of the approach of the input disturbance, and was governed by the number of stages employed. It is significant that the effects of an increased number of stages is so definitely illustrated by the impulse response. Relating the impulse response, or rtdf, back to the cumulative distribution function, the "tail" of the rtdf corresponds to the approach to steady state in the step-change response (see figs. 14, 15). The forward portion of the impulse response is related to the break-away of the step response from the initial steady state condition. The height of the peak is determined by the maximum slope of the step response curve.

A realization of how the perfectly mixed tray assumption affects the mixing response can, therefore, be demonstrated by fitting the impulse function. This is related to the condition that the derivative of an n^{th} order response to a step change is zero at the inlet boundary, while this is not true for a first order response. Therefore, the practice of simply ignoring the fact that a response is multi-stage by representing a step change response by a dead-time plus a first order response may be shown to be vastly in error by examining the impulse response. The implication here is, that of the three most common methods of dynamic testing, transient or step-change response techniques are perhaps the least informative of the three. It has long been acknowledged that frequency response was inherently the best method because the frequency spectrum could be examined, however, it is a difficult technique to employ. Pulse testing is somewhat less difficult but offers a better approach to study of mixing

effects than transient response, such that the additional difficulty may be rewarded.

Moments of the distribution

The Laplace transform for the general mixing response to a step-change is for n stages with n-1 equal is:

$$\mathcal{L}\left[F(t)\right] = \frac{1}{L(\phi s+1)(Ts+1)^{n-1}} = \frac{(1/T^{n-1}\phi)}{s(s+\frac{1}{\phi})(s+\frac{1}{T})} \qquad 93$$

The impulse response, or rtdf, in Laplace transform notation then is the moment generating function:

$$\mathcal{L}\left[F(t)\right] = \frac{(1/T^{n-1}\ \phi)}{(s+\frac{1}{\phi})(s+\frac{1}{T})} \qquad 94$$

By application of equation 74, the r^{th} moment about the origin, μ'_r, may then be determined by evaluating the r^{th} derivative of the generating function at s=0. The following are equations for the first four moments with respect to the origin for the case of n perfectly mixed stages with (n-1) stages equal:

$$\mu'_1 = \left[(n-1)T + \phi\right] \qquad 95$$

$$\mu'_2 = \left[(n)(n-1)T^2 + 2(n-1)T\ \phi + 2\phi^2\right] \qquad 96$$

$$\mu'_3 = \left[(n+1)(n)(n-1)T^3 + 3(n-1)T^2\phi + 6(n-1)T\phi^2 + 6\phi^3\right] \qquad 97$$

$$\mu'_4 = \left[(n+2)(n+1)(n)(n-1)T^4 + 4(n+1)(n)(n-1)T^3\phi + 12(n)(n-1)T^2\phi^2 + 24(n-1)T\phi^3 + 24\phi^4\right] \qquad 98$$

The results of the simulation and calculation of the moments of the residence time distribution function are presented in table 2.

Examination of the mean residence time reveals some channeling of liquid occurred, as shown by the fact that the peaks of the distribution

Table 2. Simulated mixing response characteristics

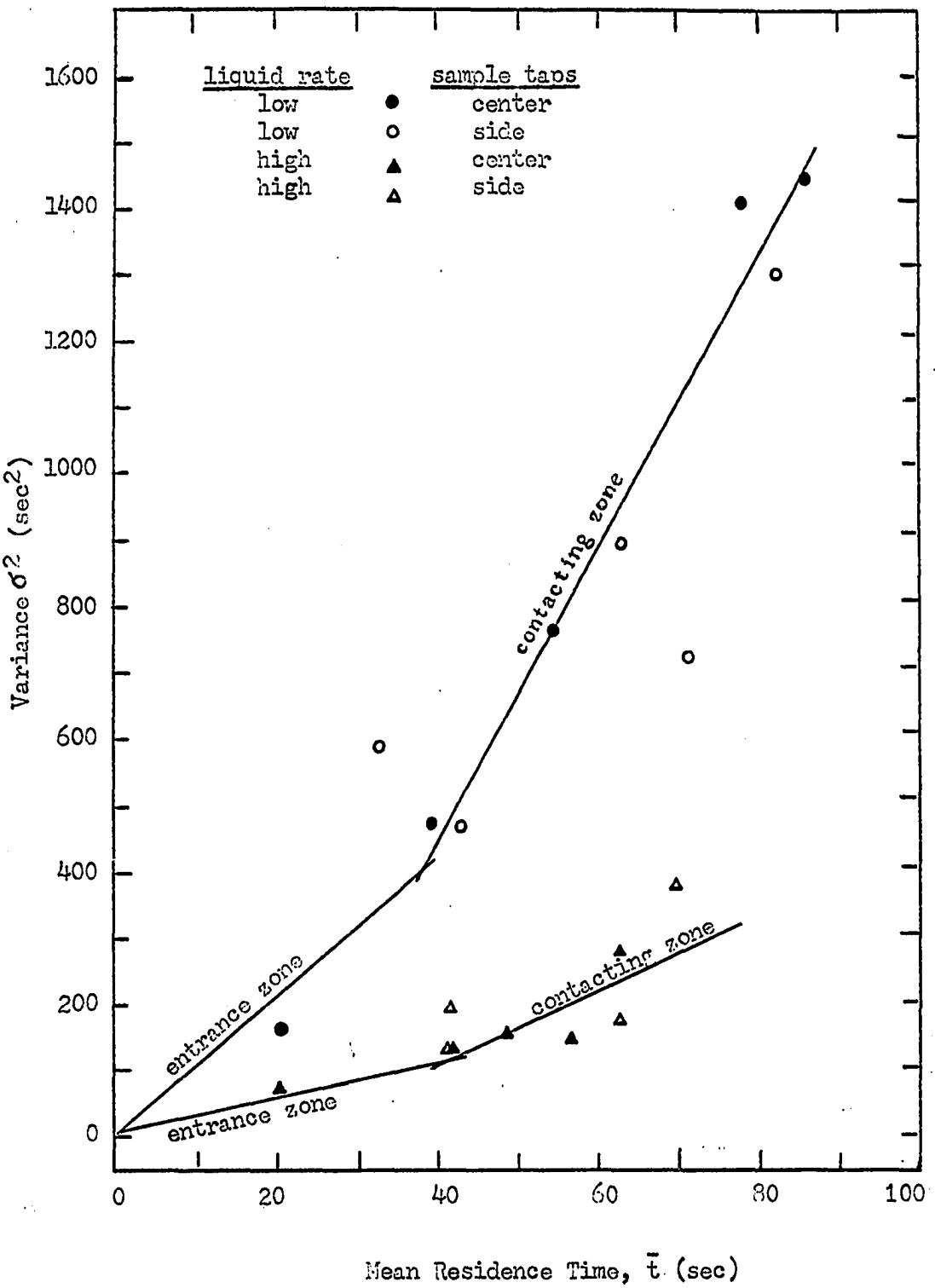
Liquid Flow Rate and Sample Profile	Total Number Stages	Time Constants (n-1) Equal Stages T (sec)	Time Constants Unequal Stage ϕ (sec)	Dead Time (sec)	Mean Residence (no dead time) μ_1 (sec)	Mean Residence (with dead time) $\bar{t}$ (sec)	Variance μ_2 or σ^2 (sec^2)	Coefficient of Variation σ/μ	Skewness $\alpha_3 = \frac{\mu_3}{\sigma^3}$	Kurtosis $\alpha_4 = \frac{\mu_4}{\sigma^4}$
Low Center 1	2	6	11.2	3.5	17.2	20.7	162	0.74	1.54	6.98
2	3	6	20	7.5	32.0	39.5	472	0.68	1.63	7.35
3	3	6	26.1	16.5	38.1	54.6	753	0.72	1.76	7.94
4	5	6	35.4	18.5	59.4	79.9	1398	0.63	1.73	7.83
5	6	6	35.4	20.5	65.4	85.9	1434	0.58	1.67	7.60
Low Side 1	3	6	18.8	2.5	30.8	33.3	576	0.67	1.62	7.26
2	4	6	18.8	6.5	36.8	43.3	459	0.58	1.48	6.67
3	5	6	27.3	11.5	51.3	62.8	887	0.58	1.60	7.27
4	6	6	23.1	17.5	53.1	70.6	713	0.50	1.41	6.41
5	6	6	33.3	18.5	63.3	81.8	1289	0.57	1.64	7.46
High Side 1	2	4.28	21.4	5.0	25.7	30.7	478	0.85	1.89	8.53
2	3	4.28	11.1	22.0	19.7	41.7	133	0.59	1.98	9.59
3	6	4.28	10	10.0	31.4	41.4	192	0.43	3.28	4.91
4	10	4.28	15.0	16.0	53.6	69.6	384	0.37	1.24	4.58
5	10	4.28	4.3	20.0	42.9	62.9	180	0.31	0.80	4.50
High Center 1	3	3.75	6.3	7	13.9	20.9	69	0.60	1.21	4.89
2	8	3.75	6.0	10	32.3	42.3	134	0.36	0.74	6.04
3	9	3.75	6.0	13	36.0	49.0	149	0.34	0.70	9.67
4	10	3.75	3.75	19	37.5	56.5	141	0.32	0.615	4.23
5	10	3.75	10.9	18	44.7	62.7	275	0.35	0.90	8.46

function occurred before the mean residence time. This is consistent with results reported by Foss (31), at the lower of two flow rates. The phenomena described as by-passing and dead-space are closely related, although Levenspiel (60) clearly distinguishes between the two. By-passing is presented as the case where a fraction of inlet material appears instantaneously in the output, while dead-space is characterized by a fraction of material remaining in the system for a considerable period of time. Both cases, however, involve channeling since one fraction of material has a relatively shorter residence time than the remaining fraction. The distinction is the relative time required for inlet material to reach the outlet. The situation reported by Foss, as well as results reported here, would therefore fit the description of dead-space. It also does not follow that a system characterized by dead-space will necessarily experience by-passing with increased flow rate. Further results of Foss, for a much higher flow rate, reduced the dead space condition, except in the vicinity of the inlet. Results of the current study indicate similar dead-space conditions occurred at both flow rates. Levenspiel (60) also presented a method for estimating the fraction of dead-space, but commented that further mathematical analysis of this condition is difficult.

Eddy diffusion correlation

The variance, σ^2, or second moment about the mean for the residence time function was plotted versus the mean residence time, $\bar{t}$, in fig. 31, for both liquid flow rates. The data points corresponding to sample locations 2 and 5 were represented quite well by straight lines fitted by least squares techniques. By employing the correlation of the rate of

Fig. 31. Rtdf variance versus mean residence time


liquid rate
low
low
high
high
sample taps
center
side
center
side
1600
1400
1200
1000
800
600
400
200
0
Variance σ² (sec²)
contacting zone
entrance zone
contacting zone
entrance zone
0
20
40
60
80
100
Mean Residence Time, t̄ (sec)

increase of the variance with the tray distance, the eddy diffusion coefficient was calculated for each flow rate. The good fit of the straight line to the points, especially at the low flow rate, is tantamount to a constant diffusion coefficient across the contacting zone. This constitutes a verification of the relationship employing rate of increase of the variance as a mixing parameter. Foss (31) presented similar results, but did not have simultaneous sampling at all tray locations, thereby requiring a separate run for each sample location, and introducing slight variations in froth velocity. To account for the entrance zone effects, a straight line was fitted to the points for sample locations 1 and 2 and a different diffusion coefficient calculated for both liquid rates. The entrance zone, prior to the bubble-caps, was previously noted to be well-agitated, but a different bulk flow rate and lack of obstructions contribute to the different value of the diffusion coefficient. The results are summarized in table 3.

Table 3. Values of the diffusion coefficient

Zone	Low Liquid Rate			High Liquid Rate		
	V_f(ft/sec)	D_E(ft^2/sec)	N_{Pe}	V_f(ft/sec)	(ft^2/sec)	N_{Pe}
Entrance	0.0112	0.495×10^{-3}	6.21	0.0118	0.23×10^{-3}	12.75
Contacting	0.0216	5.37×10^{-3}	4.02	0.049	7.07×10^{-3}	6.93

Transient Composition Response

Experimental

The response to a step-change in acetone composition was investigated at the two levels of liquid flow rate studied in the mixing tests. The complete collection of experimental data, including operating conditions, is presented in the appendix. Typical composition response curves for each of the flow rates are plotted in figs. 32 and 33. A comparison of the composition responses for the center and side series of sample locations is shown in figs. 34 and 35 for each level of liquid rate. Data shown in the latter two plots are based upon collection of ten samples simultaneously, by special adaptation of the sample collection system. The subsequent analysis of various mathematical models was made for the center series of sample taps only, based on the similarity of results with those of the series of taps along each side of the tray.

An experimental determination of the vapor composition profile above each tray revealed a slight gradient did exist at both liquid rates. The vapor composition transient was also examined, and estimated to be roughly approximated by a first order response as shown in figs. 36 and 37.

Tray model evaluation

The specific models were formulated based upon the varied mixing assumptions, as discussed. Several additional pieces of information were necessary for a complete mathematical description. These are all based upon the relationship between vapor and liquid phases. All of the models were written in terms of the changes in the liquid phase, therefore each required a means of relating vapor input and output changes to liquid effects. A pseudo-equilibrium curve technique such as that of Lamb

Fig. 32. Typical transient composition response, low liquid rate, 0.6 gpm

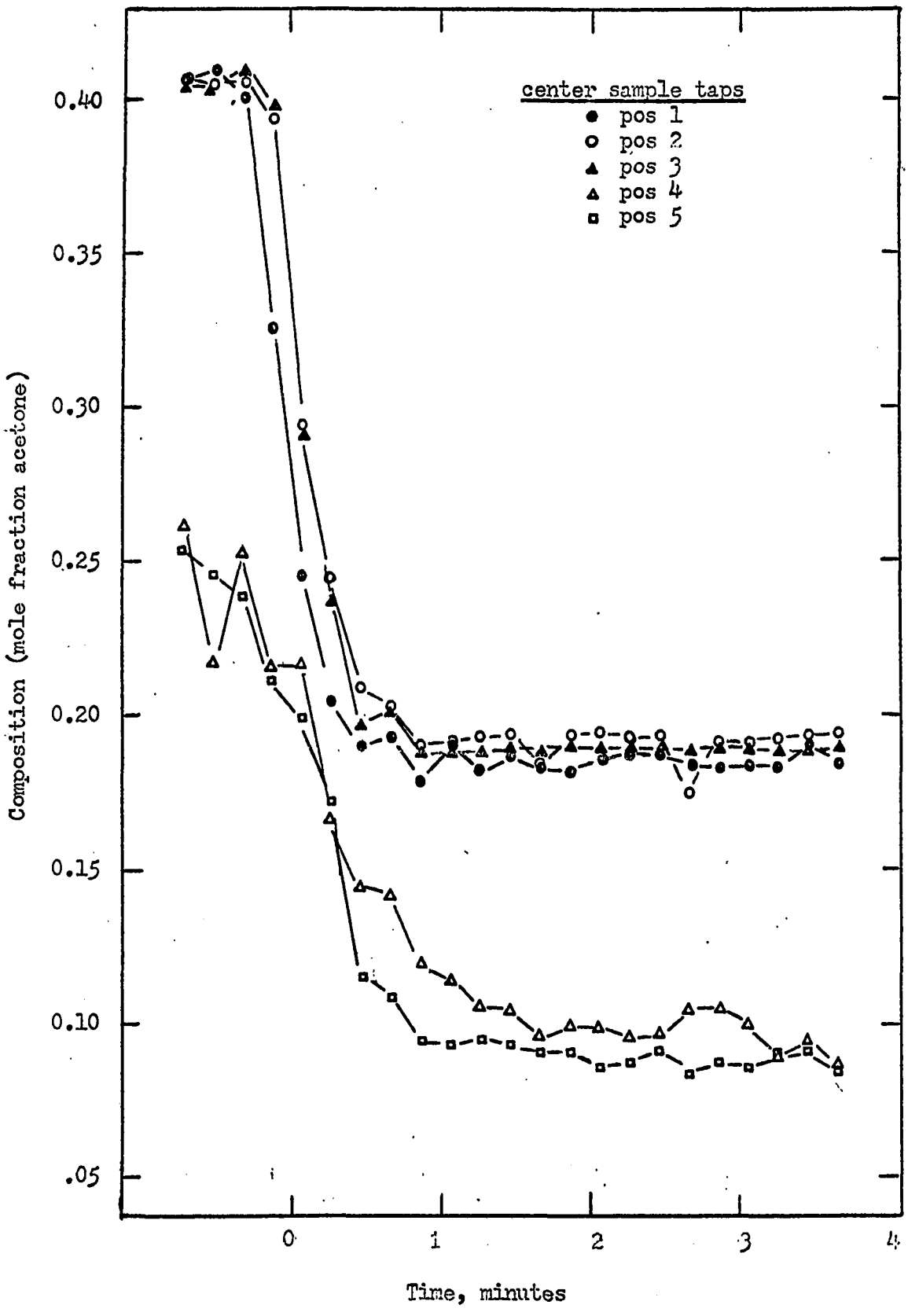

center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
0.40
0.35
0.30
0.25
0.20
0.15
0.10
.05
Composition (mole fraction acetone)
0
1
2
3
4
Time, minutes

Fig. 33. Typical transient composition response, high liquid rate, 0.9 gpm

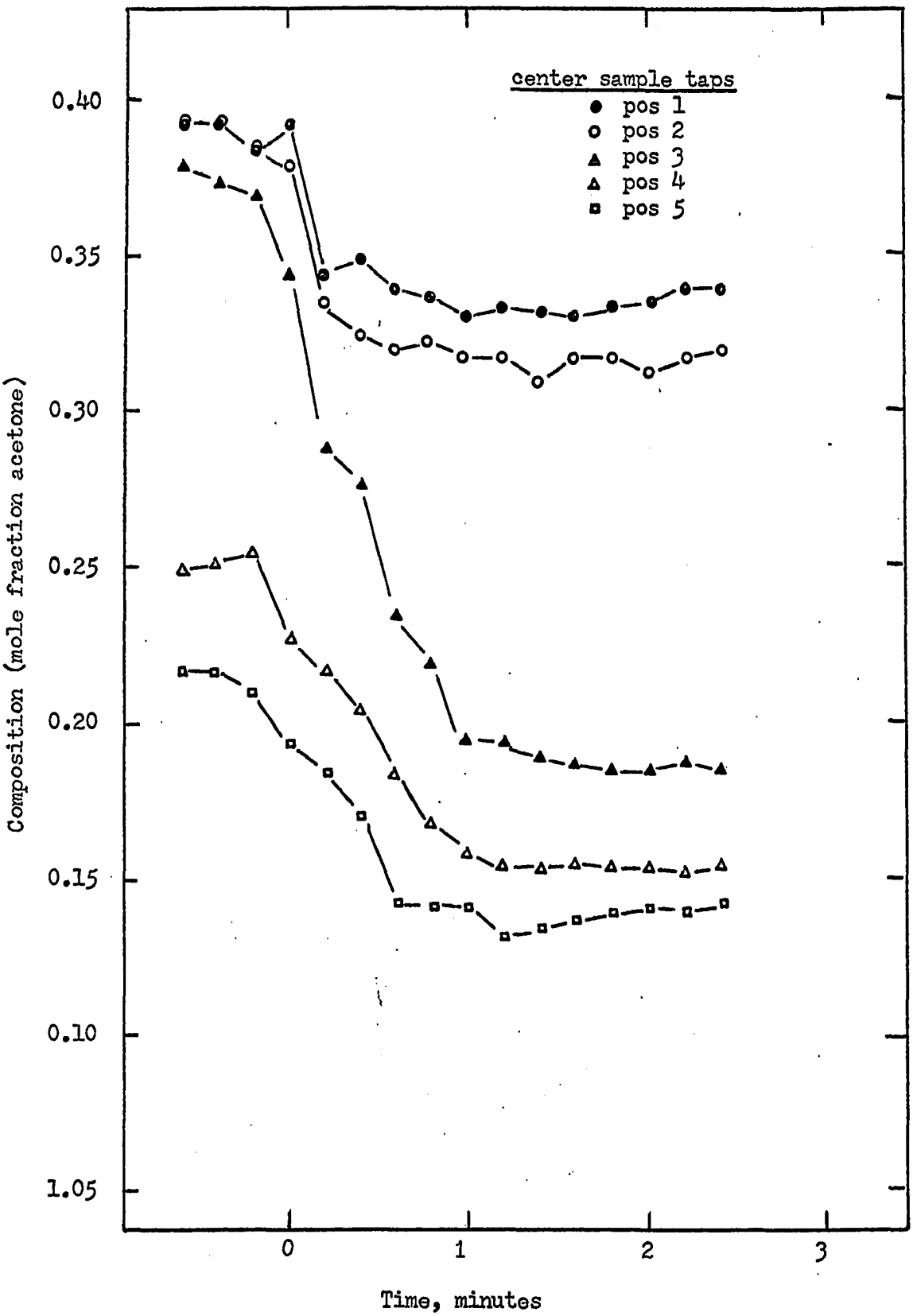
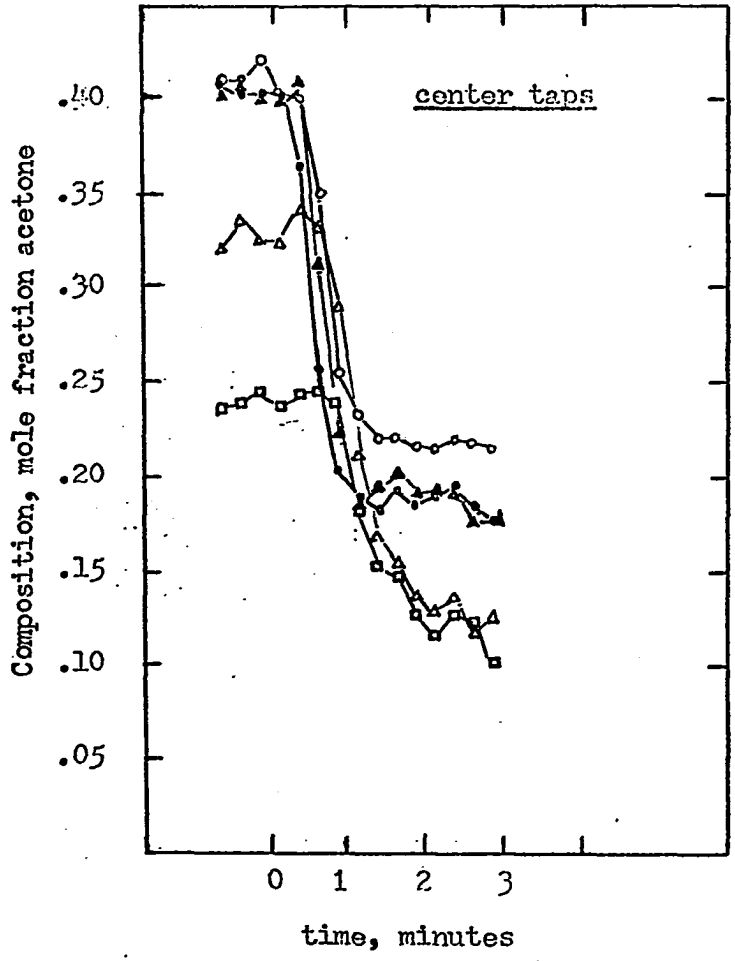

center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
0.40
0.35
0.30
0.25
0.20
0.15
0.10
1.05
Composition (mole fraction acetone)
0
1
2
3
Time, minutes

Fig. 34. Transient composition response comparison of center and side series of sample locations at low liquid rate, 0.6 gpm


center taps
Composition, mole fraction acetone
.40
.35
.30
.25
.20
.15
.10
.05
0
1
2
3
time, minutes

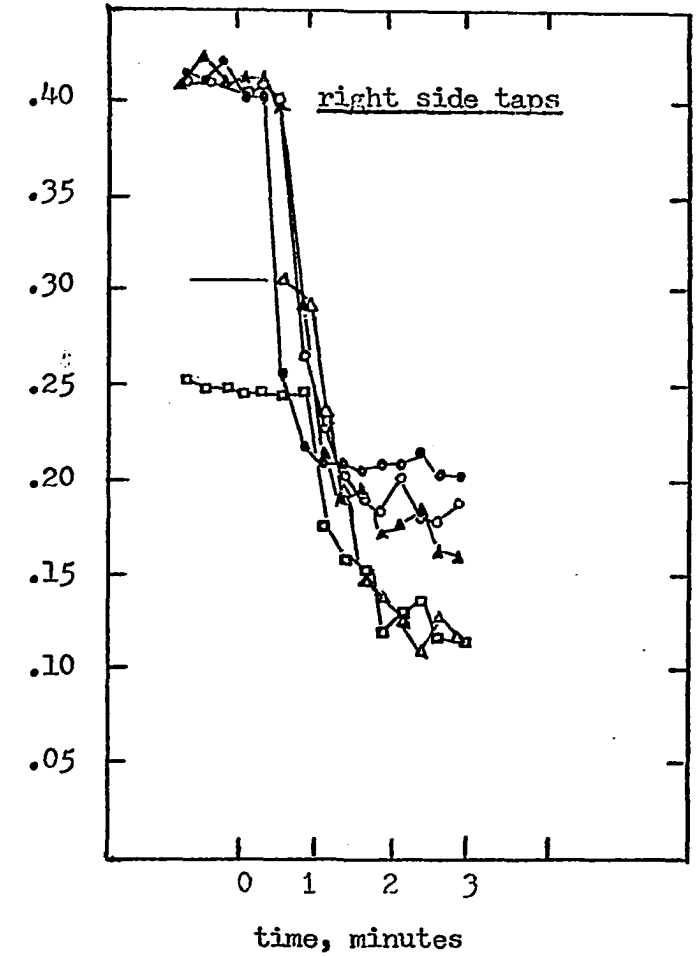

right side taps
.40
.35
.30
.25
.20
.15
.10
.05
0
1
2
3
time, minutes

Fig. 35. Transient composition response comparison of center and side series of sample locations at high liquid rate, 0.9 gpm

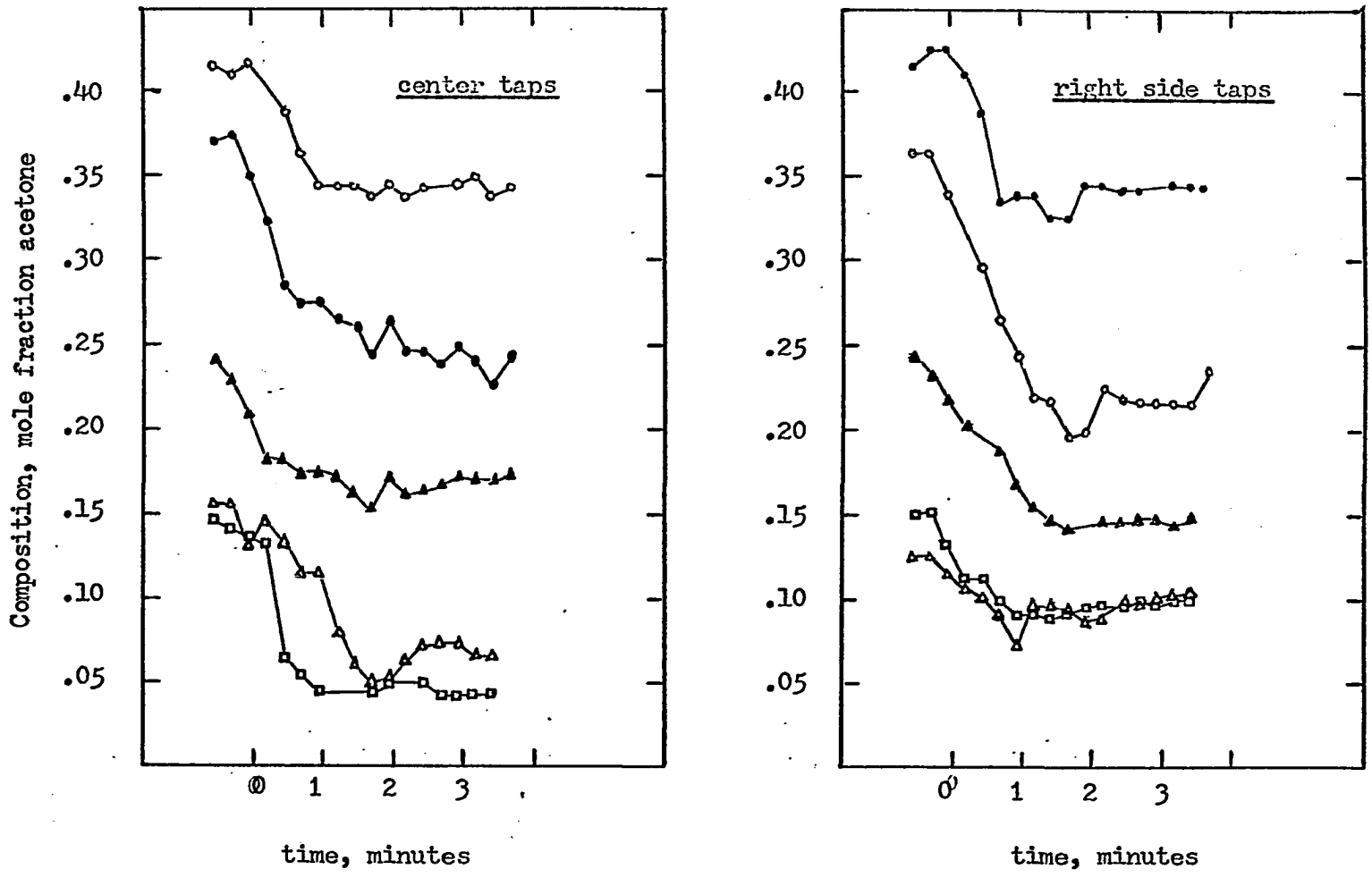
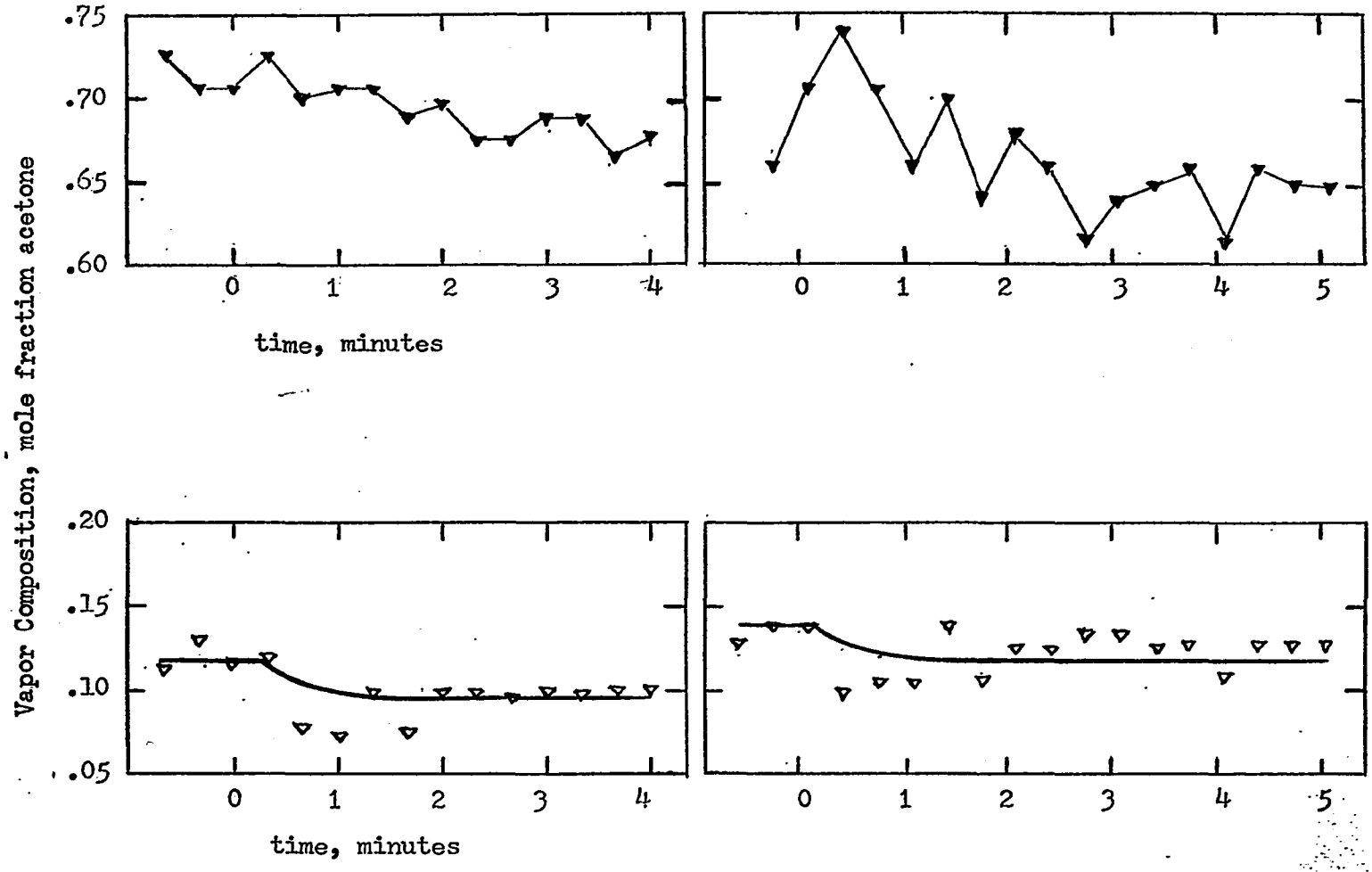

center taps
right side taps
Composition, mole fraction acetone
.40
.35
.30
.25
.20
.15
.10
.05
0
1
2
3
time, minutes

Fig. 36. Vapor composition response at low liquid rate

a. test tray output response
b. test tray input response showing curve

Fig. 37. Vapor composition response at high liquid rate

a. test tray output response
b. test tray input response showing simulated curve


Vapor Composition, mole fraction acetone
.75
.70
.65
.60
.20
.15
.10
.05
0
1
2
3
4
5
time, minutes
time, minutes

et al. (57) was chosen. Experimental tray efficiencies were observed to be in the range of 80%. Based upon this information a pseudo-equilibrium curve was formed by reducing the values on the vapor-liquid equilibrium curve presented in fig. 1 to 80% of their original value. For each sample location, an average pseudo-equilibrium coefficient, K, was determined by taking the slope of the chord connecting initial and final steady state values. The coefficients which were employed for both flow rates are presented in table 4.

Table 4. Pseudo-equilibrium coefficient values

Sample location	K
1	0.125
2	0.125
3	0.125
4	0.252
5	0.410

The pseudo-equilibrium technique related vapor output terms, but the vapor input was handled differently. Detailed sampling of the lower tray was not attempted, since primary attention was focused upon the test tray behavior, and not upon overall column dynamics. Therefore, to avoid reliance upon mathematical description of the lower tray, the vapor input was approximated by a first order response with sutiable time delay, for all models studied. Although perfectly mixed vapor was not assumed, the vapor composition change was assumed to be equal across the tray. The models were written in terms of deviations from steady state, i.e. zero initial conditions on time, which made the above mentioned assumption adaptable. The earlier discussion concerning downcomer lag affects the composition response

models, since it was desired to formulate a model representing the tray separate from the downcomer. A more desirable experimental situation would have had the step-change imposed at the tray entrance zone, that is, without a downcomer mixing effect. To accomplish a fair evaluation of the models, the imposed disturbance function for each was assumed to be identical to the function which represented the experimentally measured composition response at sample location 1. The function was simulated by the perfectly-mixed model, based upon the number of stages determined in the mixing tests. To conserve computer components, the function was not generated each time by the original analog computer program, but rather was initially stored for later use in a ten-point variable diode function generator.

The mathematical solutions of the four models considered were accomplished on the analog computer. The models involving the assumptions of perfect mixing, either single stage or multi-stage, were represented by ordinary differential equations, as discussed. Solution of such equations by analog computation is quite common. The models involving plug flow, with or without diffusion, were previously shown to be distributed parameter systems, that is, were represented by partial differential equations. The solution of these equations was handled by the finite difference methods, specifically, dividing the space domain into discrete steps. By application of these techniques, a parallel solution of the overall equation was carried out, i.e. solved as a time function for all space points simultaneously. Analog programming was simplified by formulation of a general computer equation which required only one patch-panel

to be wired, with alterations for each model made by potentiometer settings (see fig. 38). The general equation took the form:

$$\frac{dx_i}{dt} = Ax_{i+1} - Bx_i + Cx_{i-1} + Dy_{j-1} \qquad 99$$

x = liquid composition, mole % acetone
y = vapor composition, mole % acetone
t = time, sec

where the parameters (A, B, C, D) are different constants based upon the (mixing and mass transfer) characteristics of each model. In some models certain of the parameters were zero. The parameters in coefficient form for each model are listed in table 5.

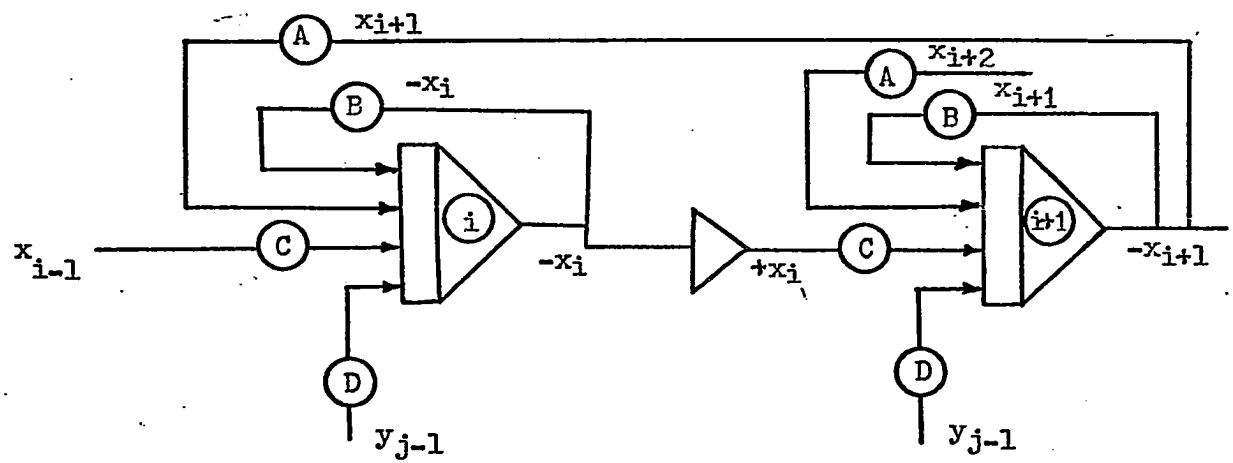
Table 5. Coefficients for computer equation representing composition response

Model	A	B	C	D
Single stage perfect mixing	0	$\left(\frac{1 + \lambda\bar{K}}{\bar{t}_o}\right)$	$\left(\frac{1}{\bar{t}_o}\right)$	$\left(\frac{\lambda}{\bar{t}_o}\right)$
Multi-stage perfect mixing	0	$\left(\frac{n + \lambda K_i}{n\bar{t}_i}\right)$	$\left(\frac{1}{\bar{t}_i}\right)$	$\left(\frac{\lambda}{n\bar{t}_i}\right)$
Plug flow	0	$\left(\frac{n + \lambda K_i}{\bar{t}_o}\right)$	$\left(\frac{n}{\bar{t}_o}\right)$	$\left(\frac{\lambda}{\bar{t}_o}\right)$
Plug flow with diffusion	$\left(\frac{n^2 D_E}{S_o^2} - \frac{N}{2\bar{t}_o}\right)$	$\left(\frac{2n^2 D_E}{S_o^2} + \frac{\lambda K_i}{\bar{t}_o}\right)$	$\left(\frac{n^2 D_E}{S_o^2} + \frac{n}{2\bar{t}_o}\right)$	$\left(\frac{\lambda}{\bar{t}_o}\right)$

The multi-stage perfect mixing, or pool concept, model was set up with the number of stages and residence time for each based upon the mixing response simulations. For each stage, the following equations may be written:

$$\bar{t}_i \frac{dx_i}{dt} = -\left(1 + \frac{K_i}{n}\right)x_i + x_{i-1} + \left(\frac{\lambda}{n}\right) y_{j-1} \qquad 100$$

Fig. 38. Analog computer program for generalized composition response equation


A
x_{i+1}
B
$-x_i$
C
x_{i-1}
i
$-x_i$
D
y_{j-1}
$+x_i$
A
x_{i+2}
B
x_{i+1}
C
i+1
$-x_{i+1}$
D
y_{j-1}

where $\bar{t}_i = (h_i/L)$ 101

i = stage number from inlet
j = tray number from bottom
$\bar{t}_i$ = mean residence time, i^{th} stage, sec
h_i - volumetric accumulation, i^{th} stage, ft^3
n = number of stages
= G/L
G = vapor rate, lb-moles/sec
L = liquid rate, lb-moles/sec
K_i[2] = pseudo-equilibrium coefficient at i^{th} stage
$\bar{K}$ = mean K_i

The solution for the response at each sample location required a separate computer solution, due to different mixing response simulations for each. The single stage perfect mixing model may then be formed from the above equation by letting $n = 1$, $t_i = \bar{t}_o$, and $K_i = \bar{K}$, where K is an average of individual K values. Only the tray output response is predicted by the resulting equation:

$$\bar{t}\, dx_j = -(1+K)x_j + x_{j+1} + (\lambda)y_{j-1} \qquad 102$$

The plug flow model is formed from the partial differential equation discussed earlier by applying finite difference methods to the space derivative. Let the following backward difference equation:

$$\frac{\partial x(t)}{\partial S} = \frac{x_i - x_{i-1}}{\Delta S} = \frac{x_i - x_{i-1}}{S_o/n} \qquad 103$$

S = tray distance, ft
S_o = overall tray length, ft
ΔS = finite difference step length, ft

be substituted in the equation:

$$\left(\frac{\bar{t}_o}{S_o}\right)\frac{\partial x}{\partial t} = -\frac{\partial x}{\partial S} - \left(\frac{\lambda K_i}{S_o}\right)x \qquad \left(\frac{\lambda}{S_o}\right)y_{j-1} \qquad 104$$

which yields:

$$(\bar{t}_o)\frac{dx}{dt} = -(n + K\lambda)\, x_i + x_{i-1} + (\lambda)\, y_{j-1} \qquad 105$$

The equation was solved by standard analog computer a representation of 10-step finite difference approximation. The response for various tray locations was determined by monitoring the solution at the appropriate difference step. The number of steps was limited by the available computer components. Iteration methods would have permitted a greater number of stages, but storage of intermediate results could only be accomplished by use of the variable diode function generators (vdfg). The error introduced by the repeated use of the vdfg for storage would not have presented a significant improvement in the 10-step approximation. The results of decreasing the step size by an order of ten was briefly examined and indicated only slight error. The comparison between the pool concept model and pure plug flow must be emphasized. In the limiting case, the models are exactly equal when the tray is divided into a number of perfectly-mixed pools approaching infinity. As solved on the analog computer, the plug flow solution is an approximation of the true result. The parameters (see table 5) for solution of the two models, indicate that for the pool concept model when all stages are equal, i.e. $\bar{t}_i = \bar{t}_o/n$, the result is equivalent to the plug flow approximation made with a similar number of finite difference stages. The only difference in the two solutions, therefore, is that the number of size of the individual stages were determined from the mixing response simulation. The plug flow equation when modified

to account for back-mixing by eddy-diffusion mechanism appears as follows:

$$\left(\frac{\bar{t}_o}{S_o}\right)\frac{\partial x}{\partial t} = \left(\frac{D_E}{V_f}\right)\frac{\partial^2 x}{\partial S^2} - \frac{\partial x}{\partial S} - \left(\frac{\lambda K}{S_o}\right)x + \left(\frac{\lambda}{S_o}\right)y_{j-1} \qquad 106$$

D_E = eddy diffusion coefficient, ft^2/sec
V_f = froth velocity, ft/sec

The partial space derivatives may be replaced by the following finite difference approximations:

$$\frac{\partial x(t)}{\partial S} = \frac{x_{i+1} - x_{i-1}}{2\Delta S} = \frac{x_{i+1} - x_{i-1}}{(2S_o/n)} \qquad 107$$

$$\frac{\partial^2 x(t)}{\partial S^2} \qquad \frac{x_{i+1} - 2x_i + x_{i-1}}{(\Delta S)^2} \qquad \frac{x_{i+1} - 2x_i + x_{i-1}}{(S_o^2/n^2)} \qquad 108$$

The overall equation then may be rearranged as follows:

$$\bar{t}_o \frac{dx_i}{dt} = \left[\frac{n^2}{N_{Pe}} - \frac{n}{2}\right] x_{i+1} - \left[\frac{2n^2}{N_{Pe}} + \lambda K_i\right] x_i + \left[\frac{n^2}{N_{Pe}} + \frac{n}{2}\right] x_{i-1} + (\lambda) y_{j-1} \qquad 109$$

where $$N_{Pe} = \frac{V_f S_o}{D_E} = \frac{S_o^2}{D_E \bar{t}_o} \qquad 110$$

The diffusion equation required a two-part solution since the diffusion coefficient in the entrance zone was estimated to be different from that in the contacting zone. Each section was solved by a 10-step finite difference solution of the equation presented. The output function for the entrance zone was stored by the variable diode function generator for later use as an input to the contacting zone equations.

A major difficulty in solution of the diffusion equation results from the application of boundary conditions. The equations for all of the models are expressed as dynamic equations, i.e. they represent deviations from steady state. As such, the initial condition for time in each case is zero composition change. Again the input function for each model is the

same, and this represents a space boundary condition. Although the input function and its derivatives may be written analytically, the finite difference solution required imposition of the output boundary equation. Since it is desired to predict the output function by employing the model, some alternate assumption must be made for solution. In this case for the last stage in the approximation the substitution is made of $x_i + 1 = x_i$ where $i = n$. This is equivalent to the assumption of the partial space derivative, $\frac{\partial x}{\partial S}$, equal to zero for the $(n + 1)^{st}$ stage, and the following finite difference approximations result, for the n^{th} stage:

$$\frac{\partial^2 x(t)}{\partial S^2} = \frac{-x_i + x_{i-1}}{(\Delta S)^2} = \frac{-x_i + x_{i-1}}{(S_o^2/n^2)} \qquad 111$$

$$\frac{\partial x(t)}{\partial S} = \frac{x_i - x_{i-1}}{2\Delta S} \qquad \frac{x_i - x_{i-1}}{2S_o/n} \qquad 112$$

On the analog computer, the situation is characterized by replacement of the feedback from the forward integrator by that of a feedback signal from the last (n^{th}) integrator. In terms of the physical system the assumption is that there is slight difference between 2 points near the end of the system. This is not an unrealistic approximation.

The possibility of serial solution of the partial differential equation would not have alleviated the difficulty. The technique would have required a finite difference approximation of the time domain with iteration. The solution would have been time-consuming, as well as, introducing the error due to repeated use of vdfg storage and re-generation. A distinct advantage of the parallel solution technique for partial differential equations is the simultaneous solution. This not only conserves computing time, but permits examination of the response at various space points in a system.

On immediate evaluation of the effects of parameters upon the responses is easily accomplished. In a serial solution, the entire solution which is itself time consuming, must be repeated several times before the parameters can be evaluated. The only drawback to the parallel solution is the large number of components involved. For example, ten step solution of the diffusion equation required 12 integrators, 30 amplifiers, 40 potentiometers, 2 vdfg's, and comparator relays. The value of hybrid computation techniques is emphasized by the handling of these equations.

Evaluation of the models by comparison with experimental results is made in figs. 39 to 45. The significant part is that all of the multi-step models are quite similar. This was not completely unexpected, since there have been previous reports of the similarity of the series perfect-mixing and diffusion model approaches. For example, Kramers and Alberda (55) in frequency response studies of a reactor compared both approaches. Not only did they report a relationship between Peclet number and the number of perfectly mixed stages, but also a distinct similarity in Bode plot representation of the two models. They did not project the strong conclusion that the models were identical. Nevertheless, the implication of the current results is that where a distributed parameter representation is necessary, the approximation realized by employing a series perfect mixer model is reasonable.

The prediction of the output response at the low flow rate was poor for all models, but within reason for the high flow rate. At both flow rates, the response at other sample locations was quite acceptable. Two possible causes for the error in output response at the low-flow rate are

Fig. 39. Transient composition response of single stage perfect mixing model at high liquid rate. Experimental data points are shown for two runs (see table 10, test 1 and table 11)

Fig. 40. Transient composition response of single stage perfect mixing model at low liquid rate. Experimental data points are shown for two runs (see table 12, tests 2 and 4)

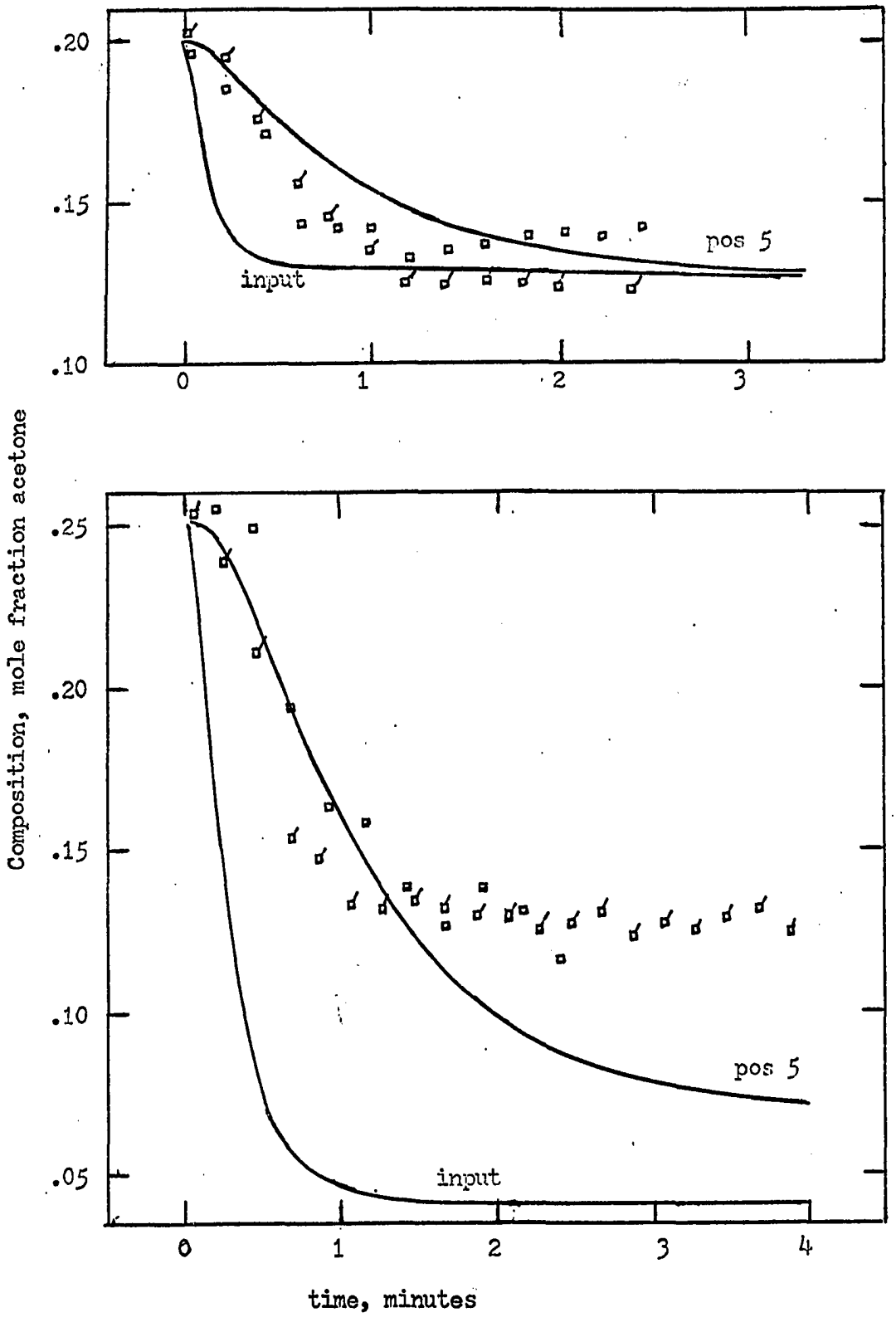

.20
.15
.10
0
1
2
3
pos 5
input
.25
.20
.15
.10
.05
0
1
2
3
4
pos 5
input
Composition, mole fraction acetone
time, minutes

Fig. 41. Transient composition response of multi-stage perfect mixing model at low liquid rate. Experimental data points are shown for two runs (see table 12, tests 2 and 4)

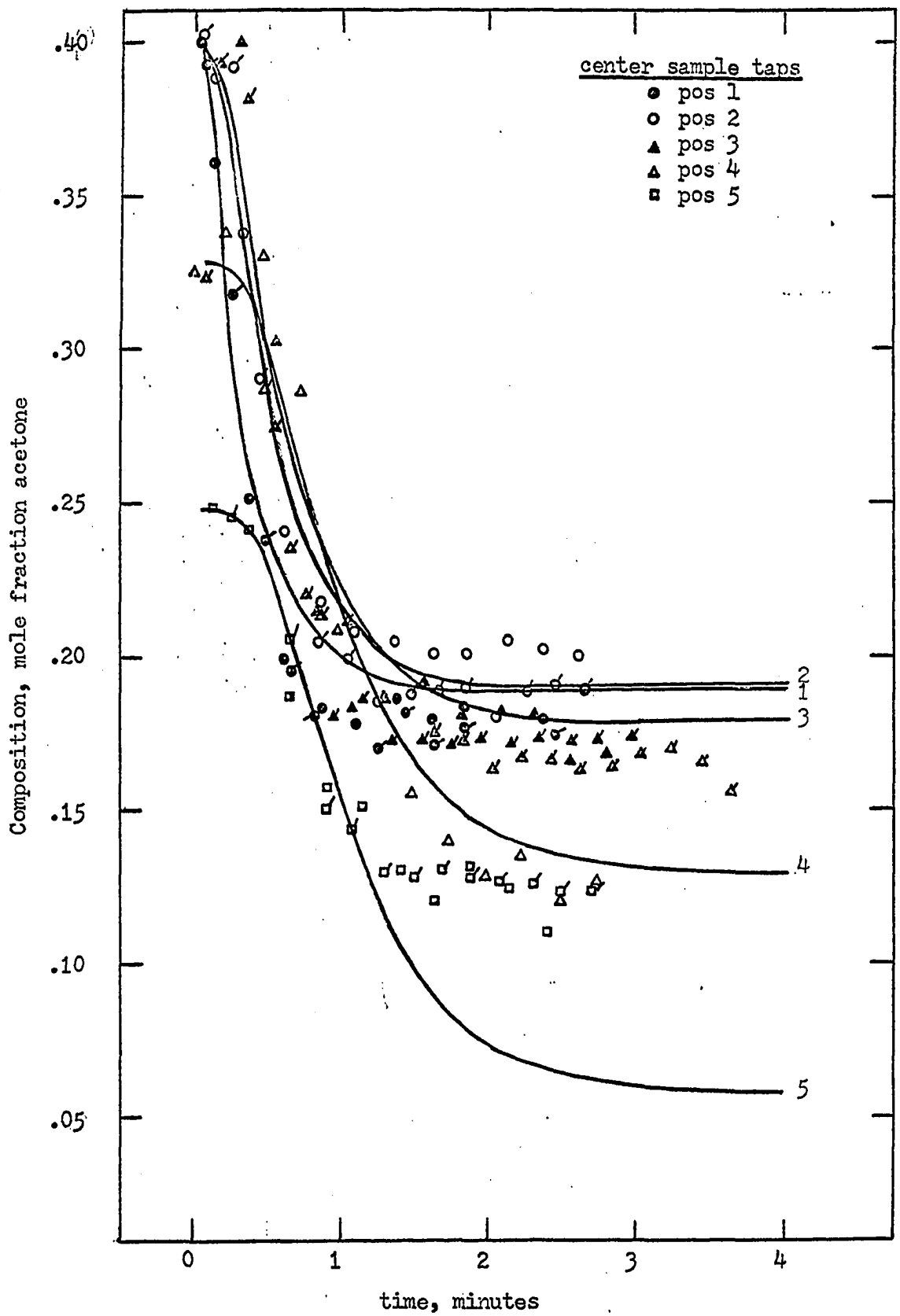

center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
Composition, mole fraction acetone
.40
.35
.30
.25
.20
.15
.10
.05
0
1
2
3
4
time, minutes
1
2
3
4
5

Fig. 42. Transient composition response of multi-stage perfect mixing model at high liquid rate. Experimental data points are shown for two runs (see table 10, test 1 and table 11)

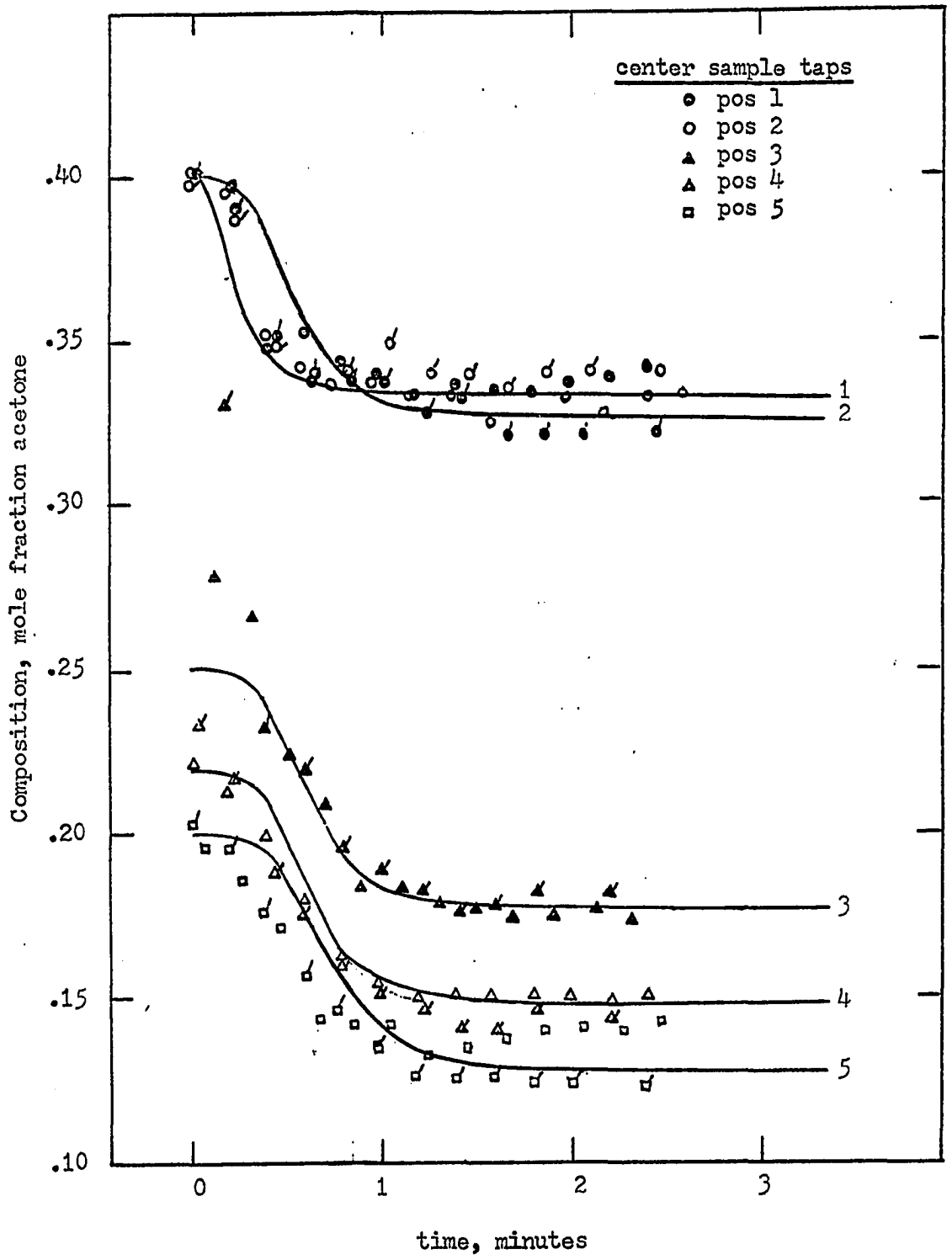

center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
.40
.35
.30
.25
.20
.15
.10
0
1
2
3
1
2
3
4
5
Composition, mole fraction acetone
time, minutes

Fig. 43. Transient composition response of plug flow model at low liquid rate. Experimental data points are shown for two runs (see table 12, tests 2 and 4)

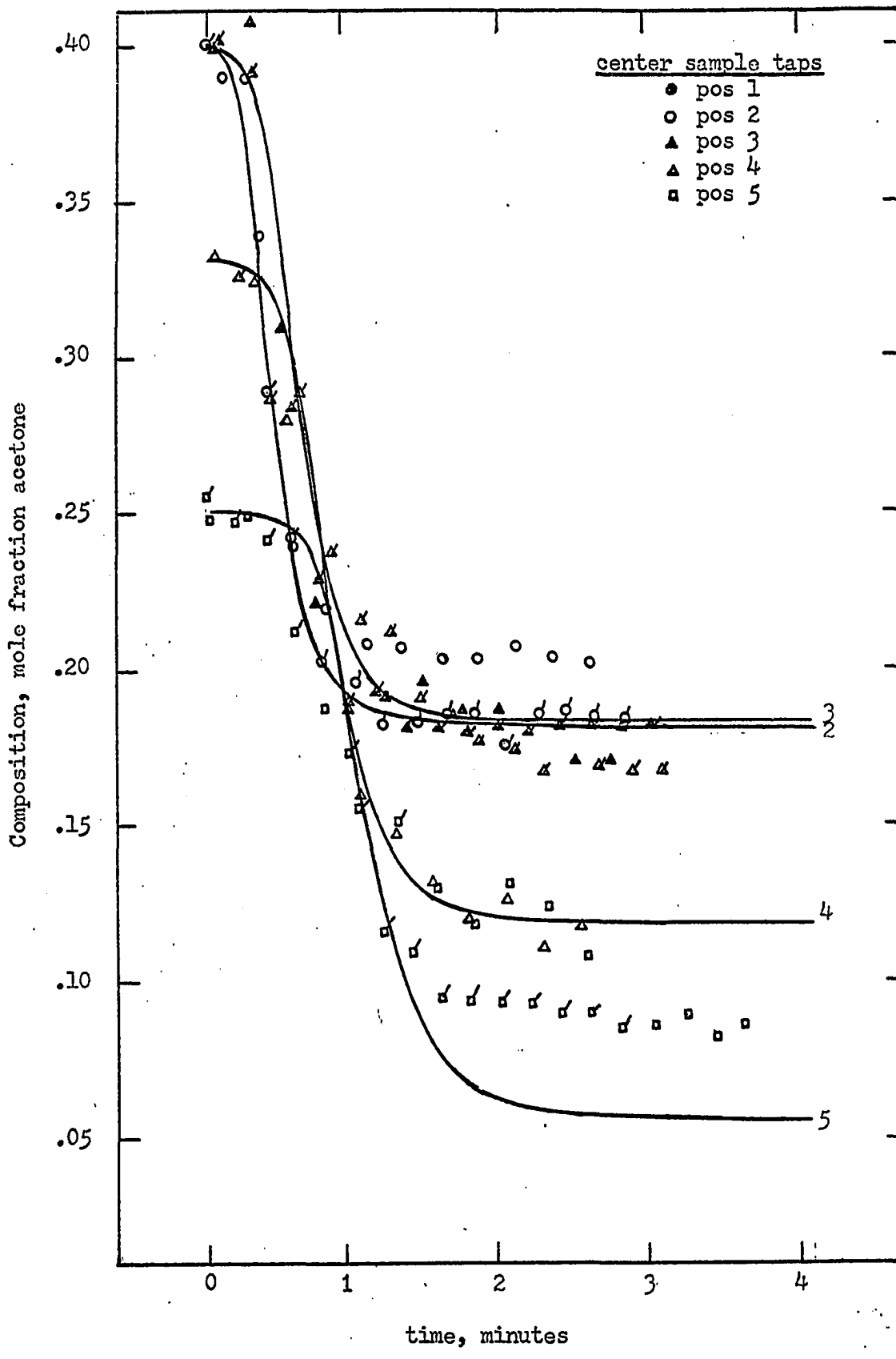

center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
.40
.35
.30
.25
.20
.15
.10
.05
0
1
2
3
4
3
2
4
5
Composition, mole fraction acetone
time, minutes

Fig. 44. Transient composition response of plug flow model at high liquid rate. Experimental data points are shown for two runs (see table 10, test 1, and table 11)

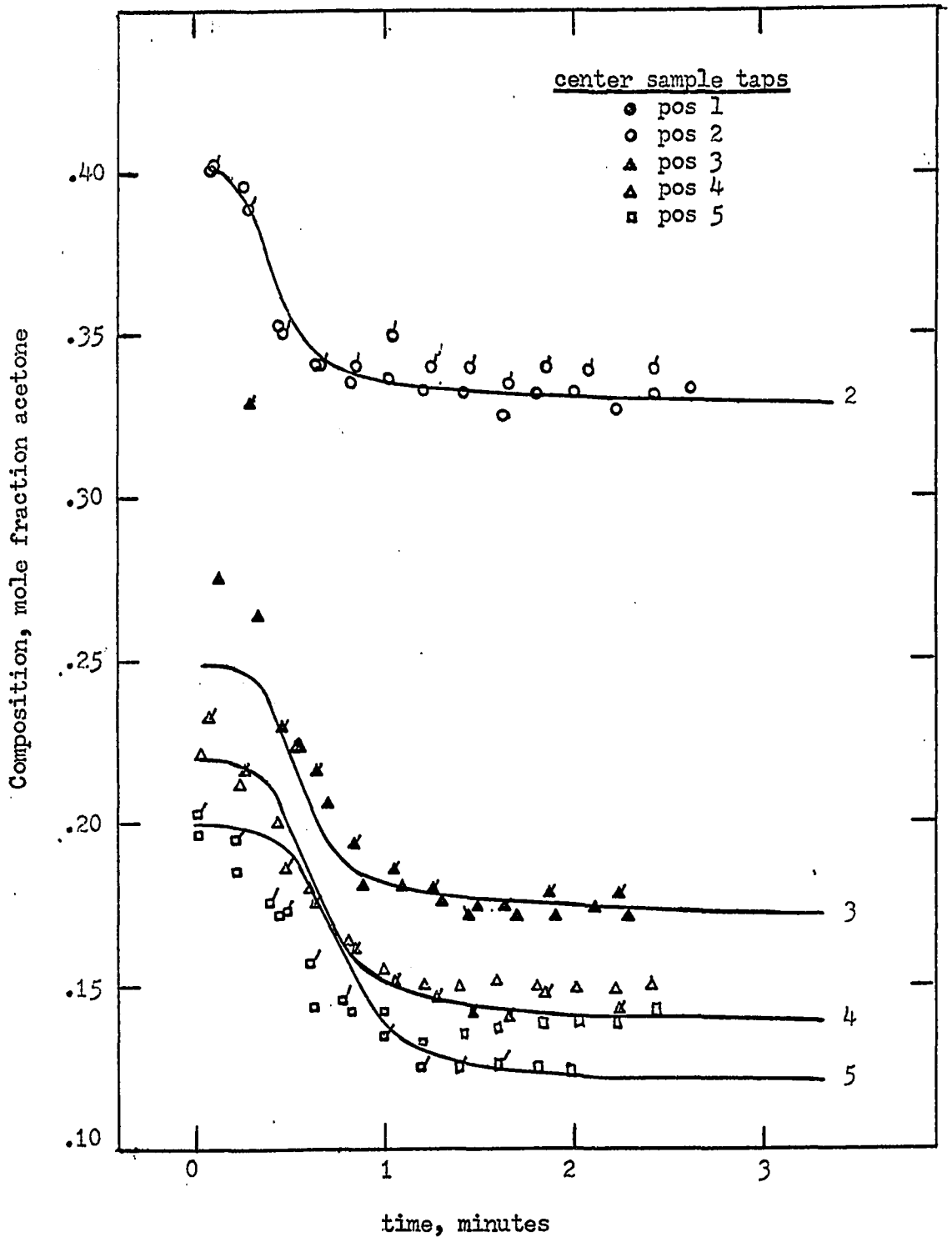

center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
.40
.35
.30
.25
.20
.15
.10
0
1
2
3
2
3
4
5
Composition, mole fraction acetone
time, minutes

Fig. 45. Transient composition response of plug flow with diffusion model at low liquid rate. Experimental data points are shown for two runs (see table 12, tests 2 and 4)

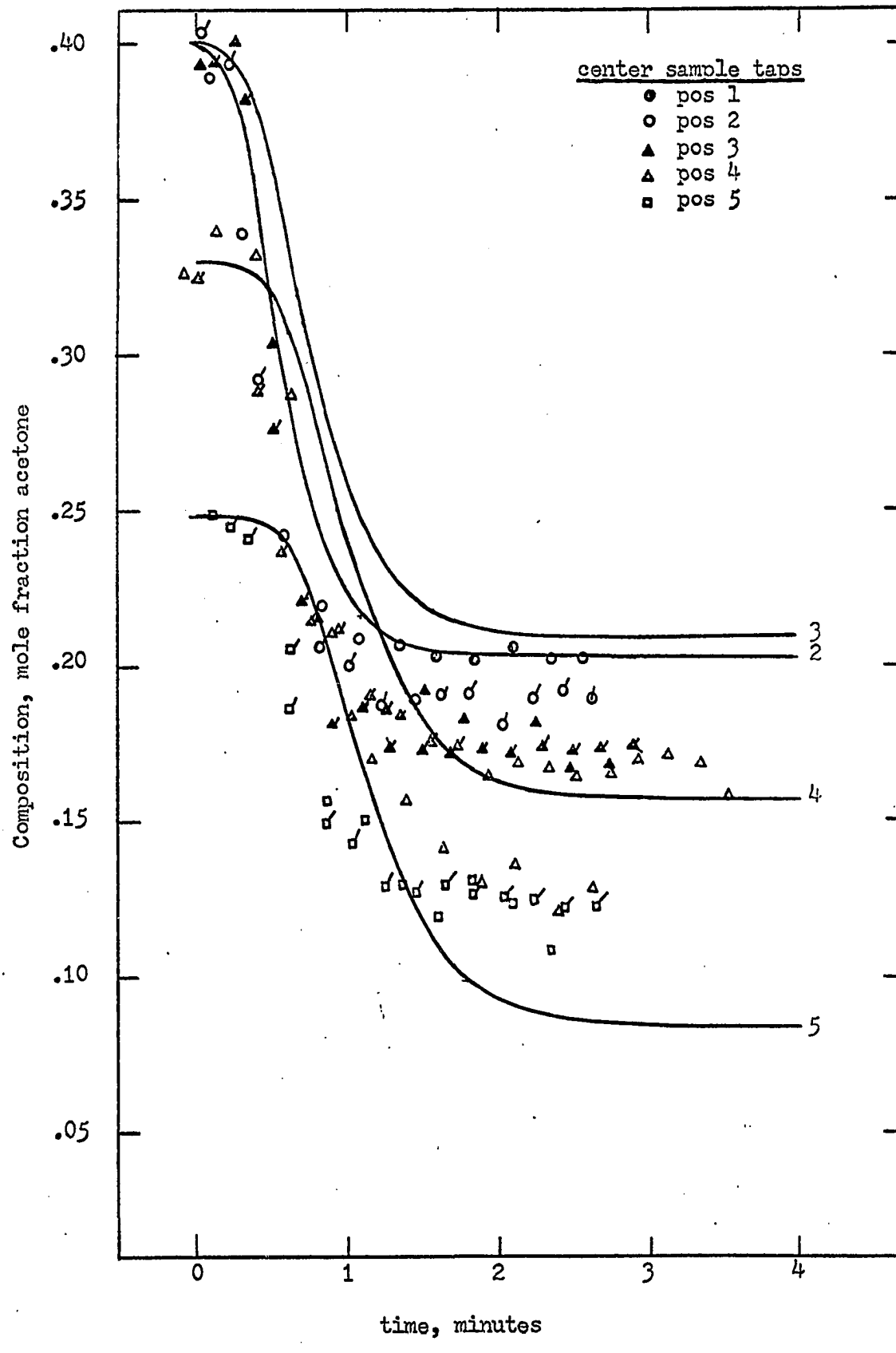
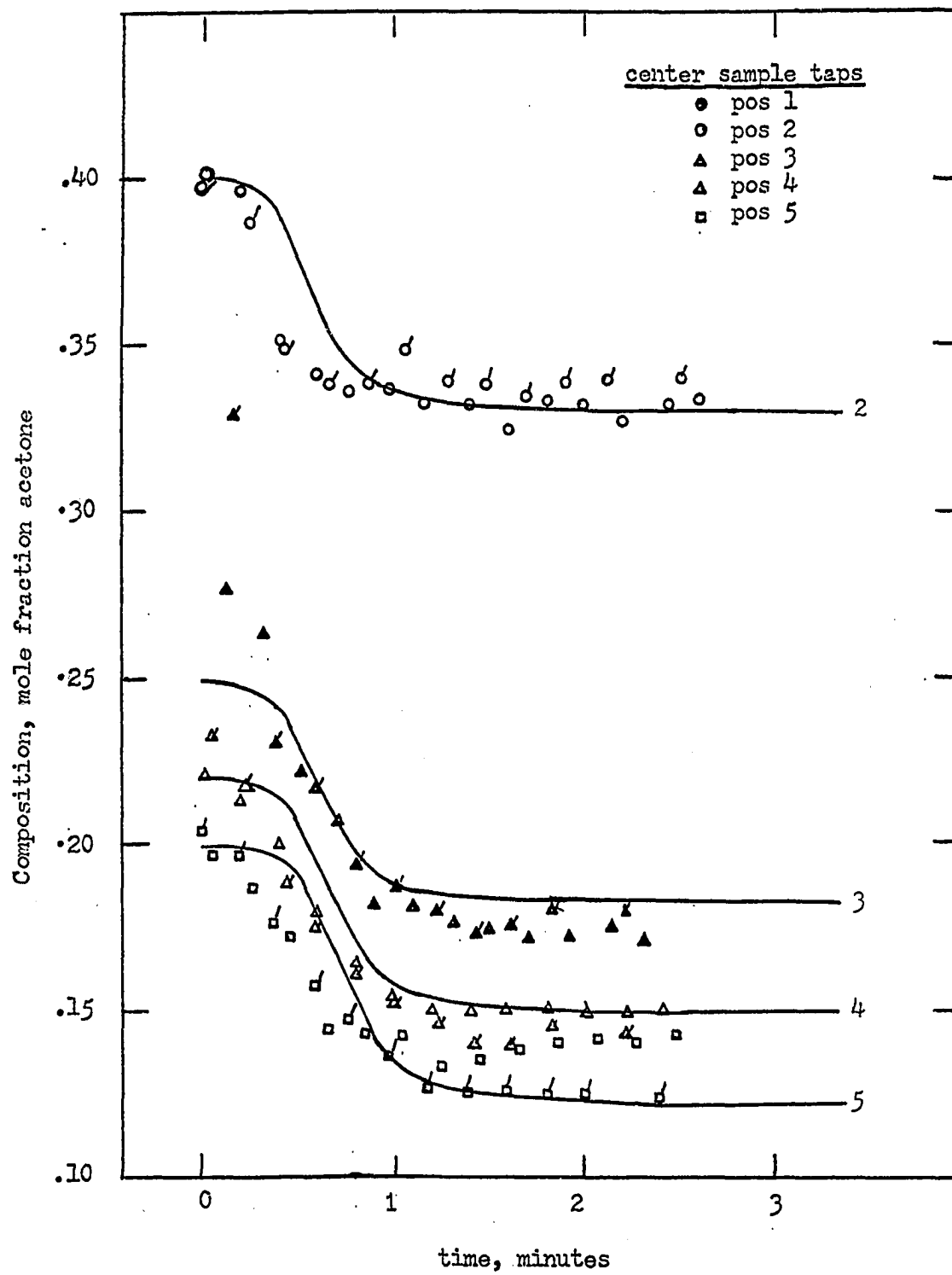

center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
.40
.35
.30
.25
.20
.15
.10
.05
0
1
2
3
4
3
2
4
5
Composition, mole fraction acetone
time, minutes

Fig. 46. Transient composition response of plug flow with diffusion model at high liquid rate. Experimental data points are shown for two runs (see table 10, test 1 and table 11)


center sample taps
pos 1
pos 2
pos 3
pos 4
pos 5
.40
.35
.30
.25
.20
.15
.10
0
1
2
3
2
3
4
5
Composition, mole fraction acetone
time, minutes

the indication of channeling or error in pseudo-equilibrium coefficient. The channeling might have introduced liquid of higher composition to the output sample location but not to other locations. The pseudo-equilibrium technique is at best an approximation, and easily in error if the experimental conditions do not agree. The alternative, however, is introduction of a non-linear equilibrium relationship leading to a variable coefficient differential equation. This is not a very attractive approach from the standpoint of complexity.

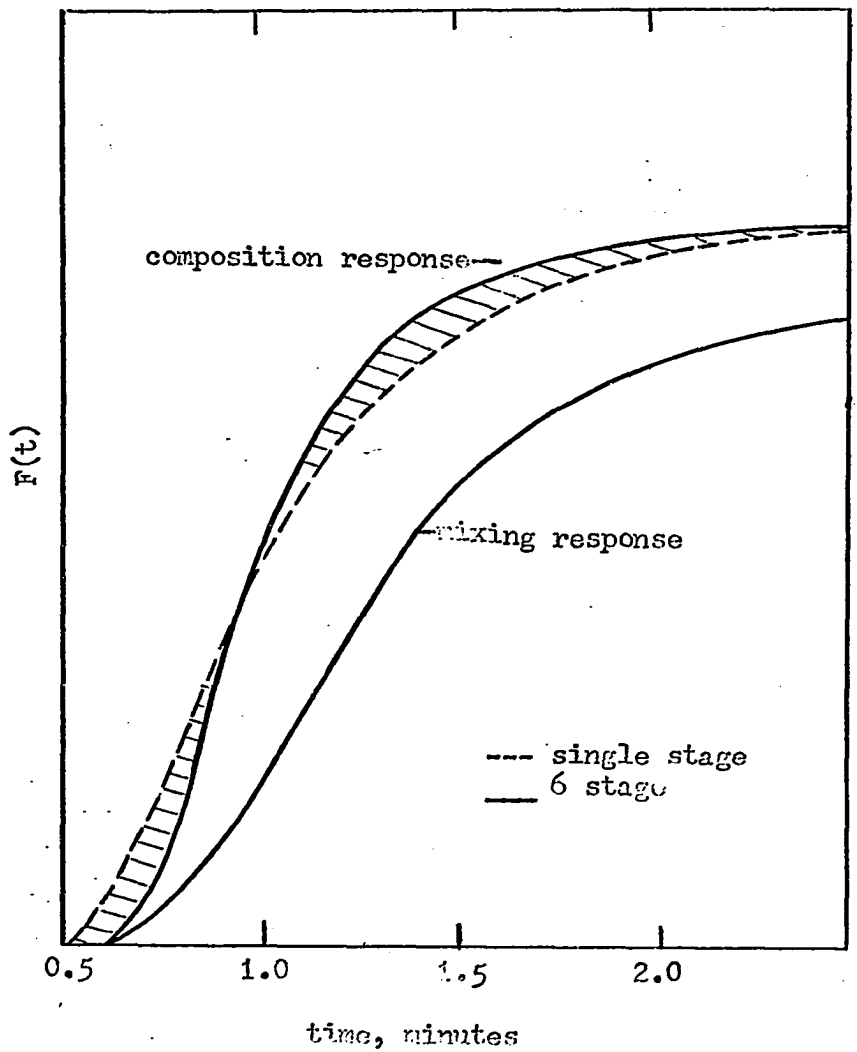
Comparison of the series perfect mixer model and the single stage perfect mixer model indicates a more gradual response by the single stage as expected. The experimental results, however, appear to fit a multi-stage model in the breakaway portion of the response. The importance of fitting this section of the response curve, discussed under the mixing-effects, is best seen by examination of the impulse response.

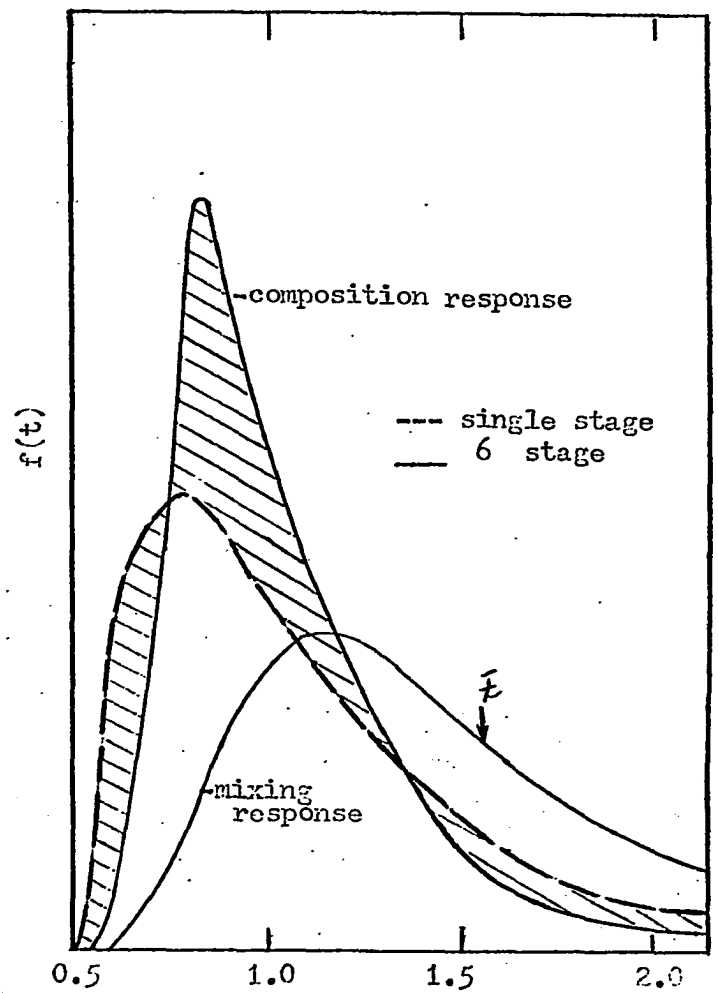
The plot shown in fig. 46 demonstrates the effects upon both the step and the impulse composition responses of portraying a distillation plate as a single perfectly mixed stag. Comparison is made between the responses predicted by a perfectly-mixed pool-concept model and a single perfectly-mixed stage model with error shown as the shaded area between the curves. Since mass transfer effects are similar for these models, the area between the curves is analogous to the "segregation" concept for a mixing parameter as presented by Danckwerts (25). Also presented in the above-mentioned figure are both the impulse and step mixing response curves, which serve to demonstrate the separate relative contribution to the overall composition response by both the mixing effects and mass transfer effects. The step response curve comparison indicates that the overall composition response

Fig. 47. Comparison of overall composition response and the mixing response of a six-stage perfect-mixing model with the overall composition response of a single-stage perfect-mixing model

a. Step-change response

b. Impulse response


composition response
mixing response
--- single stage
___ 6 stage
F(t)
0.5
1.0
1.5
2.0
time, minutes


composition response
--- single stage
___ 6 stage
mixing response
f(t)
t̄
0.5
1.0
1.5
2.0

is faster and has a higher gain than the mixing response. The gain change is dependent upon the net transfer from a system, since a pure mixing system has unity gain, i.e. no net depletion or accumulation of material. The mixing effects appear in the breakaway portion and the slope of the step response. In the impulse composition response, the relative height of the peak is governed by both the number of mixing stages and the net mass transfer. This representation of composition response data can be considered from a statistical sense since they also represent residence time functions. In this case, however, a particle is subject to mass transfer which alters residence time and dispersion as reflected by the moments. These concepts are more frequently applied to reaction systems, but should bear examination for possible value in description of mass transfer parameters not studied here.

As mentioned previously, assumption of a distillation tray acting as a single perfectly mixed stage has been common. Neglecting imperfect mixing effects, in this manner, can lead to serious error. The reason for such an assumption, which involves approximating a multi-order response by a first order model, has been one of expediency. The simplification of a model representing a complete distillation column is apparent when each tray is reduced to a single mixing lag. The adequacy of such representation must be questioned, in particular for commercial columns whose diameters often exceed several feet. The economics of solution of such a problem also must be considered. If a complete column model with each tray represented by a multi-stage model were to be simulated, the computer hardware required would be exceedingly great. Hybrid computation would most likely provide the best approach. In such a solution, the ability

to replace the diffusion equation with a series perfect mixer model would represent a considerable advantage.

CONCLUSIONS AND RECOMMENDATIONS

1. Analog computer simulation of an experimental mixing response on a distillation tray by a series of perfectly mixed elements proved to be satisfactory. The simulated mixing response was used in the development of a model to represent composition dynamics under conditions where mass transfer was taking place. Comparison of the predicted composition response with experimental results indicated agreement.
2. A model assuming plug flow of liquid across the tray offered no significant improvement in predicted composition response over that obtained with the series perfect-mixer model.
3. An eddy diffusion coefficient, determined from the mixing analysis, was incorporated into a plug flow model. Comparison with experimental results revealed that the model gave no significant improvement in predicted composition response over the plug flow or series perfect mixer model.
4. A model based upon a single perfectly mixed stage provided the least accurate representation of the transient composition response. A distributed parameter model, such as those discussed in 1, 2, and 3 above, is thus preferred, to account for imperfect mixing effects upon the composition response.
5. The impulse response technique for evaluation of mixing effects offers many advantages because of the direct presentation of the residence time distribution function. Simulation of the mixing response by a series of perfectly mixed increments permitted subsequent analytical

calculations, e.g. determination of the moments of the distribution function.

6. The distinction between first-order and multi-order mixing effects is best illustrated by the impulse response. Approximation of a multi-order mixing system by a first-order model can lead to serious error.

7. The correlation of rate of increase of variance of residence time distribution function with tray distance was verified for the contacting zone of the tray. The relationship affords a convenient method for calculation of an eddy diffusion coefficient.

8. It is recommended that a study be made of the effects upon overall column dynamics, due to representation of the tray by a distributed parameter model of the series perfect-mixer type.

9. The analysis of residence time distribution functions, such as the comparison of mixing and composition impulse responses, is suggested for possible correlation of other operational variables. Many of the current correlations are based upon steady state results, and could be greatly enhanced by the information revealed by unsteady state analysis.

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NOMENCLATURE

b = lateral tray coordinate

D_E = eddy diffusivity, ft^2/sec

$E(t)$ = expected value of $t = \bar{t}$

$F(t)$ = cumulative distribution function

$f(t)$ = residence time distribution function

G = vapor flow rate, moles/minute

H = liquid holdup, moles

h = vapor holdup, moles

i = stage number

j = tray number

K = pseudo-equilibrium coefficient

L = liquid flow rate, moles / minute

n = number of stages

N_{Pe} = Peclet number = $(\frac{V_f S_o}{D_E})$

s = Laplace transform variable

S = longitudinal coordinate

S_o = overall tray length, ft

T = time constant for equal stages

t = time, sec

$\bar{t}$ = mean residence time, sec

V_f froth velocity or bulk flow rate, ft/sec = $S_o/\bar{t}$

w = dimensionless longitudinal tray distances = S/S_o

x = liquid composition, mole fraction

y = vapor composition, mole fraction

$\bar{y}_1$ = mean vapor composition

z = vertical coordinate

α_3 = skewness parameter = $\frac{\mu_3}{\sigma^3}$

α_4 = kurtosis parameter = $\frac{\mu_4}{\sigma^4}$

γ = coefficient of variation = $\frac{\sqrt{\mu_2}}{\mu_1}$

θ = dimensionless time = $\frac{t}{\bar{t}} = \frac{t}{(H/L)}$

$\bar{\theta}$ = 1 = dimensionless mean residence time

μ'_r = r^{th} moment about origin

μ_r = momont about mean

ρ'_f = froth density, moles/linear ft

$\sigma 2$ = variance

λ = mG/L

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APPENDIX

Table 6. Experimental mixing response data
Low liquid rate (0.6 gpm) - side sample taps

time (sec)	Relative Dye Concentration C/C_{max} pos 1	pos 2	pos 3	pos 4	pos 5
-	0	0	0	0	0
0	0	0	0	0	0
15	0	0	0	-	0
30	.020	0	0	0	0
45	.27	.16	.025	.005	.003
60	.45	.44	.24	.135	.13
75	.53	.565	.395	.37	.385
90	.57	.63	.55	.55	.615
105	.57	.685	.59	.71	.73
120	.58	.69	.615	.805	.82
135	.60	.72	.68	.84	.90
150	.61	.805	.795	.90	.92
165	.61	.705	.67	.92	.935
180	.61	.685	.69	.93	.95
195	.61	.74	.705	.975	.98
210	.60	.72	.72	.95	.975
225	.61	.72	.69	.95	.98
240	.60	.795	.685	.95	.975
255	.60	.75	.71	.99	1.00
270	.60	.75	.74	.99	1.00
285	.59	.765	.73	1.0	.96
300	.60	.72	.75	.99	.99
315	.60	.765	.765	.975	.99
330	.60	.75	.75	.975	1.00
345	.60	.75	.75	.99	.99

Table 7. Experimental mixing response data
Low liquid rate (0.6 gpm) - center sample taps

time (sec)	Relative Dye Concentration C/C_{max}				
	pos 1	pos 2	pos 3	pos 4	pos 5
-	0	0	0	0	0
0	0	0	0	0	0
15	0	0	0	0	0
30	.001	0	0	0	0
45	.335	.005	0	0	0
60	.5125	.265	.08	.08	.04
75	.5725	.4125	.235	.235	.235
90	.59	.4875	.468	.468	.435
105	.6225	.66	.59	.59	.6225
120	.6225	.6225	.72	.72	.74
135	.6225	.74	.7725	.7725	.80
150	.65	.66	.8275	.8275	.88
165	.66	.72	.8525	.8525	.88
180	.66	.66	.865	.865	.93
195	.66	.69	.865	.865	.93
210	.65	.74	.865	.865	.93
225	.65	.68	.895	.895	1.00
240	.65	.72	.865	.865	.98
255	.645	.68	.895	.895	.945
270	.645	.72	.865	.865	.96
285	.65	.66	.87	.87	.98
300	.64	.66	.865	.865	.98
315	.64	.64	.89	.89	.96
330	.6225	.70	.88	.88	.98
345	.65	.72	.895	.895	.96
360	.64	.72	.865	.865	.945
375	.64	.79	.88	.88	.945
390	.65	.79	.88	.88	.945
405	.66	.69	.84	.84	.945
420	.65	171	.85	.85	.945

Table 8. Experimental mixing response data
High liquid rate (0.9 gpm) - side sample taps

time (sec)	Relative Dye Concentration C/C_{max} pos 1	pos 2	pos 3	pos 4	pos 5
-	0	0	0	0	0
0	0	0	0	0	0
15	0	0	0	0	0
30	.06	0	0	0	0
45	.36	.04	.23	.07	.05
60	.35	.465	.415	.33	.29
75	.365	.29	.375	.275	.61
90	.465	.43	.505	.70	.87
105	.445	.355	.445	.82	.955
120	.465	.45	.53	.89	1.0
135	.42	.39	.515	.845	.955
150	.48	.53	.555	.925	-
165	.42	.56	.49	.91	.955
180	.52	.45	.535	.87	.97
195	.515	.61	.53	.94	.955
210	.485	.57	.515	.98	.955
225	.455	.54	.565	.94	.94
240	.46	.485	.52	.87	.94
255	.465	.49	.57	.895	.97
270	.485	.505	.52	.895	.94

Table 9. Experimental mixing response data
High liquid rate (0.9 gpm) - center sample taps

time (sec)	Relative Dye Concentration C/C_{max} pos 1	pos 2	pos 3	pos 4	pos 5
-	0	0	0	0	0
0	0	0	0	0	0
15	.105	0	0	0	0
30	.52	.25	.065	.020	.060
45	.54	.52	.455	.285	.365
60	.63	.32	.32	.455	.665
75	.64	.64	.55	.735	.80
90	.60	.55	.535	.765	.94
105	.595	.61	.61	.79	.97
120	.63	.61	.60	.82	.97
135	.61	.61	.54	.79	.97
150	.595	.65	.56	.82	1.00
165	.61	-	-	.82	.97
180	.62	-	.55	.73	-
195	.62	.65	.58	.79	.855
210	.64	.695	.62	.87	.935
225	.595	.67	.66	.88	.94
240	.60	.69	.61	.78	.935
255	.62	.745	.66	.78	.955

Table 10. Experimental composition response data
Low liquid rate (0.6 gpm) - center sample taps

time (sec)	Composition, mole fraction acetone				
	pos 1	pos 2	pos 3	pos 4	pos 5
Test 1					
0	.406	.406	.406	.262	.253
12	.410	.406	.406	.2175	.245
24	.401	.406	.410	.253	.239
36	.326	.394	.398	.216	.211
48	.246	.294	.291	.2175	.199
60	.204	.245	.237	.167	.172
72	.191	.210	.1975	.144	.115
84	.194	.203	,202	.142	.1085
96	.179	.1395	,1895	.120	.0945
108	.191	.1910	,1895	.114	.093
120	.182	.193	.188	.105	.0955
132	.187	.194	.1895	.1035	.0925
144	.183	.184	.189	.096	.091
156	.183	.193	.190	.100	.091
168	.186	.195	.1895	.099	.086
180	.188	.1925	.189	.096	.087
192	.187	.193	.191	.097	.091
104	.184	.175	.188	.105	.084
216	.183	.191	.1895	.105	.087
228	.184	.191	.1895	.100	.0855
240	.183	.193	.188	.089	.089
252	.1895	.194	.1895	.095	.091
264	.185	.194	.1895	.087	.085
276	.184	.193	.1895	.096	.087
288	.184	.1955	.190	.094	.087
300	.187	.193	.1895	.092	.088
312	.184	.193	.188	.090	.088
324	.188	.194	.189	.088	.087
336	.1875	.193	.189	.0905	.090
348	.182	.193	.189	.093	.088

Table 10. (Continued)

time (sec)	Composition, mole fraction acetone pos 1	pos 2	pos 3	pos 4	pos 5
Test 2					
0	.455	.435	.2175	.178	.169
12	.435	.4275	.200	.166	.166
24	.395	.410	.177	.163	.147
36	.254	.260	.154	.162	.121
48	.223	.228	.130	.120	.112
60	.189	.201	.132	.116	.100
72	.175	.187	.133	.112	.097
84	.174	.178	.127	.107	.096
96	.160	.175	.129	.108	.096
108	.161	.171	.128	.103	.096
120	.159	.169	.123	.104	.096
132	.159	.171	.123	.102	.092
144	.159	.169	.121	.104	.089
156	.159	.167	.117	.102	.089
168	.156	.166	.122	.111	.085
180	.158	.166	.119	.107	.088
192	.158	.166	.117	.100	.087
204	.160	.166	.116	.097	.083
216	.160	.167	.120	.094	.084
228	.160	.165	.116	.097	.090

Table 11. Experimental composition response data
Low liquid rate (0.6 gpm) - center and side sample taps simultaneously

time (sec)	Composition (mole fraction acetone)									
	pos C-1	pos R-1	pos C-2	pos R-2	pos C-3	pos R-3	pos C-4	pos R-4	pos C-5	pos R-5
-	.405	.417	.410	.410	.401	.410	.320	-	.235	.253
-	.401	.410	.410	.410	.405	.427	.335	-	.238	.248
0	.401	.422	.422	.370	.401	.410	.326	.245	.245	.248
15	.401	.401	.401	.401	.401	.410	.324	.265	.237	.245
30	.364	.401	.401	.410	.410	.410	.341	.278	.242	.246
45	.256	.254	.350	.401	.311	.398	.331	.305	.245	.245
60	.2025	.2175	.254	.264	.223	.290	.287	.290	.238	.246
75	.189	.209	.231	.2275	.189	.210	.210	.235	.1825	.1765
90	.1825	.209	.220	.201	.194	.191	.168	.195	.1525	.159
105	.192	.204	.220	.188	.201	.196	.155	.146	.148	.152
120	.184	.2075	.216	.1825	.189	.171	.1395	.138	.128	.120
135	.189	.2075	.216	.201	.188	.175	.129	.126	.116	.130
150	.194	.212	.220	.179	.191	.184	.136	.109	.1275	.138
165	.1915	.201	.217	.178	.175	.1615	.120	.128	.1215	.118
180	.177	.201	.214	.188	.175	.159	.127	.116	.104	.116

Table 12. Experimental composition response data
High liquid rate (0.9 gpm) - center sample taps

time (sec)	Composition, mole fraction acetone pos 1	pos 2	pos 3	pos 4	pos 5
Test 1					
-	.401	.401	.395	.328	.275
-	.395	.401	.395	.344	.266
-	.401	.401	.395	.313	.250
-	.395	.401	.395	.327	.263
-	.401	.401	.395	.316	.250
-	.395	.401	.395	.294	.246
-	.395	.401	.395	.305	.252
0	.401	.401	-	-	.233
10	.401	.401	.390	.313	.244
20	.401	.401	.401	.266	.213
30	.388	.401	.416	.244	.193
40	.324	.340	.375	.265	.210
50	.265	.286	.305	.210	.158
60	.265	.275	.256	.148	.107
70	.294	.288	.210	.147	.132
80	.266	.265	.222	.133	.111
90	.265	.265	.194	.119	.102
100	.263	.265	.182	.113	.101
110	.254	.263	.167	.116	.102
120	.252	.265	.166	.115	.105
130	.265	.265	.163	.116	.103
140	.246	.235	.158	.118	.1065
150	.250	.256	.153	.1165	.109
160	.263	.260	.156	.120	.105
170	.235	.256	.142	.117	.108
180	.265	.254	.159	.116	.110
190	.254	.265	.156	.121	.108
200	.265	.263	.165	.121	.112
210	.265	.263	.164	.121	.108

Table 12. (Continued)

time (sec)	Composition, mole fraction acetone				
	pos 1	pos 2	pos 3	pos 4	pos 5
Test 2					
-	.410	.401	.401	.245	.220
0	.405	.405	.405	.248	.226
10	.410	.405	.398	.237	.210
20	.400	.400	.395	.245	.216
30	.400	.405	.354	.2275	.196
40	.400	.400	.370	.237	.216
50	.370	.365	.305	.223	.197
60	.350	.345	.233	.181	.164
70	.350	.337	.212	.171	.1495
80	.345	.326	.195	.154	.139
90	.327	.326	.191	.1495	.129
100	.319	.323	.188	.143	.129
110	.310	.323	.181	.142	.128
120	.310	.322	.184	.143	.127
130	.319	.326	.177	.144	.129
140	.329	.323	.164	.142	.130
150	.350	.329	.167	.139	.129
160	.350	.330	.166	.129	.1255
170	.345	.327	.160	.130	.1205
180	.345	.323	.167	.126	.1205
190	.340	.313	.161	.128	.120
200	.340	.305	.1595	.125	.1125
210	.335	.300	.1595	.122	.112
220	.330	.302	.154	.120	.111
230	.319	.294	.154	.116	.1065
240	.319	.280	.1495	.115	.104
250	.323	.277	.1525	.107	.102
260	.327	.280	.154	.1075	.103
270	.323	.277	.154	.111	.1025

Table 12. (Continued)

time (sec)	Composition, mole fraction acetone pos 1	pos 2	pos 3	pos 4	pos 5
Test 3					
-	.416	.455	.437	.312	.262
0	.427	.416	.416	.303	.256
12	.413	.413	.413	.294	.2525
24	.310	.410	.410	.247	.210
36	.398	.398	.398	.233	.204
48	.360	.360	.345	.2175	.1825
60	.345	.350	.246	.188	.1635
72	.345	.350	.233	.178	.1535
84	.345	.360	.210	.1635	.142
96	.335	.350	.2025	.1535	.133
108	.340	.350	.196	.1485	.1325
120	.327	.345	.1895	.142	.133
132	.327	.350	.191	.142	.132
144	.327	.350	.196	.1485	.131
156	.327	.350	.196	.145	.130
Test 4					
-	.394	.394	.380	.251	.2175
0	.394	.394	.375	.2525	.2175
12	.385	.385	.370	.256	.2105
24	.394	.380	.345	.2275	.1945
36	.345	.336	.289	.2175	.185
48	.350	.325	.277	.205	.1715
60	.340	.320	.235	.184	.143
72	.3375	.3225	.219	.169	.142
84	.331	.318	.196	.145	.143
96	.334	.318	.194	.145	.132
108	.3325	.309	.189	.1545	.134
120	.331	.318	.184	.1565	.137
132	.334	.318	.1895	.154	.139
144	.3325	.313	.1925	.154	.141
156	.340	.318	.184	.1525	.1385
168	.340	.320	.1895	.155	.143

Table 13. Experimental composition response data
High liquid rate (0.9 gpm) - center and side sample taps simultaneously

time (sec)	Composition (mole fraction acetone)									
	pos R-3	pos C-4	pos R-4	pos C-5	pos R-5	pos C-1	pos R-1	pos C-2	pos R-2	pos C-3
-	.242	.1575	.1275	.147	.152	.370	.416	.416	.364	.240
0	.233	.1575	.1275	.141	.152	.375	.427	.410	.364	.229
15	.219	.133	.116	.1375	.133	.350	.427	.416	.339	.209
30	.2025	.148	.1065	.132	.111	.321	.410	.345	.282	.182
45	.143	.133	.1005	.065	.1155	.282	.3975	.3875	.297	.182
60	.190	.116	.091	.056	.0995	.274	.335	.372	.266	.175
75	.170	.116	.074	.044	.091	.277	.339	.345	.244	.175
90	.157	.079	.099	-	.091	.265	.339	.345	.219	.172
105	.149	.0605	.097	-	.0885	.260	.324	.345	.218	.161
120	.142	.050	.094	.046	.091	.244	.324	.339	.1975	.155
135	.193	.053	.088	.050	.094	.265	.345	.345	.199	.173
150	.148	.065	.089	-	.097	.249	.345	.339	.225	.161
165	.147	.073	.099	.050	.097	.247	.342	.342	.2195	.164
180	.149	.074	.102	.041	.1000	.239	.342	-	.216	.168
195	.149	.073	.105	.040	.097	.248	-	.345	.216	.172
210	.143	.069	.105	.044	.1000	.240	.345	.340	.216	.170
225	.149	.065	.105	.043	.1000	.242	.345	.342	.237	.174